PB84-220292

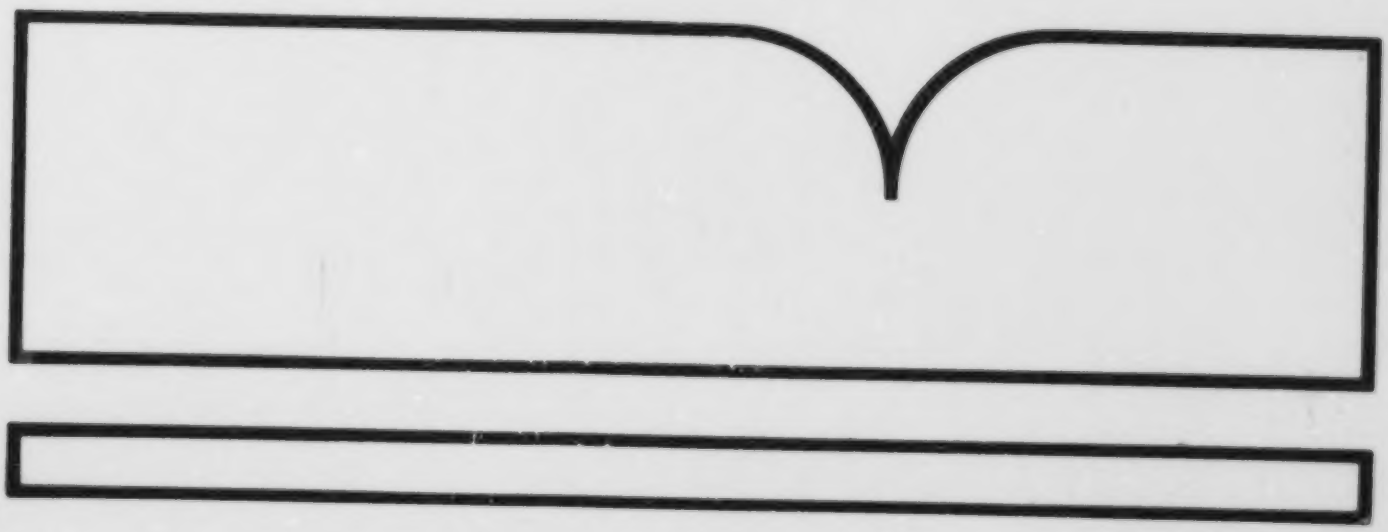
Impact of High Chemical Contaminant Concentrations on Terrestrial and Aquatic Ecosystems
A State-of-the-Art Review

Arkansas Univ., Fayetteville

Prepared for

Environmental Research Lab., Athens, GA

Jul 84



U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-220292

EPA-600/3-84-075
July 1984

IMPACT OF HIGH CHEMICAL CONTAMINANT CONCENTRATIONS ON TERRESTRIAL AND AQUATIC ECOSYSTEMS: A STATE-OF-THE-ART REVIEW

by

Louis J. Thibodeaux
Duane C. Wolf
Martha Davis
University of Arkansas
Fayetteville, AR 72701

Cooperative Agreement No. CR810480

Project Officer

George W. Bailey
Environmental Research Laboratory
Athens, GA 30613

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GA 30613

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-84-075		PB84 220292

4. TITLE AND SUBTITLE	5. REPORT DATE
Impact of High Chemical Contaminant Concentrations on Terrestrial and Aquatic Ecosystems: A State-of-the-Art Review	July 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Louis J. Thibodeaux, Duane C. Wolf, and Martha Davis	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
University of Arkansas Fayetteville, AR 72701	CBWD1A
	11. CONTRACT/GRANT NO.
	CR810480
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency--Athens GA Office of Research and Development Environmental Research Laboratory Athens, GA 30613	Final, 9/82 - 9/83
	14. SPONSORING AGENCY CODE
	EPA/600/01

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The state-of-the-art of available methods for predicting the effects of high chemical concentrations on the properties, processes, functions, cycles, and responses of terrestrial and aquatic ecosystems was reviewed. Environmental problems associated with high chemical concentrations can occur in soil and water at landfills; landfarms; spill sites; and sites where chemicals were produced, used, stored, or discarded. Considerable information is available on effects of trace chemical contaminants, such as pesticides, polychlorinated biphenyls, chlorinated hydrocarbons, and metal ions, in the respective ecosystems. Predictive techniques are becoming available to describe transport and transformation of such contaminants and, thus, their fate and distribution in certain components of the environment. Present predictive methods and models that trace transport and transformation of chemical species are based on "natural" soil and water properties such as density, porosity, infiltration, permeability, viscosity, hydrophobicity, and diffusivity. When the chemical contaminant is present in high concentrations, then the assumption of "natural" soil and water properties is suspect. The major goal of this project was to assess the research needs that will address chemical contaminants present in high concentrations in terrestrial and aquatic ecosystems.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	119
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

DISCLAIMER

Although the research described in this report has been funded wholly or in part by the United States Environmental Protection Agency through Cooperative Agreement No. CR810480 to the University of Arkansas, it has not been subjected to the Agency's peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement whould be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

FOREWORD

Environmental protection efforts are increasingly directed towards preventing adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this Laboratory's research on the occurrence, movement, transformation, and control of environmental contaminants, the impact of pollutants or other materials in soil and water is examined and environmental factors that affect water quality are assessed.

Environmental exposure to chemicals will increase as the demand for these materials increases in response to population growth. Better information about the nature of these materials and their mixtures will allow more accurate prediction of the behavior of these potentially hazardous substances in ecosystems and the development of better procedures for handling them. This report reviews research on the environmental consequences of high chemical concentrations in terrestrial and aquatic ecosystems and recommends additional studies that would provide data to better evaluate and manage contaminated systems.

William T. Donaldson
Acting Director
Environmental Research Laboratory
Athens, Georgia

PREFACE

This review is designed to report the present state of our knowledge on the impact of high concentrations of contaminants in terrestrial and aquatic ecosystems, to extrapolate that knowledge to hypothetic but plausible circumstances, and to suggest the gaps which exist in information needed to control potentially hazardous situations. This work was funded by the Environmental Protection Agency through the U.S.EPA Environmental Research Laboratory, Athens, Georgia.

The literature review here describes the present state of research which has contributed to knowledge about areas of high chemical contamination and the impact of contamination on physical, chemical, and biological properties of terrestrial and aquatic ecosystems. This information is then used in Section 3 to establish scenarios of hypothetical cases of contamination. From gaps found in data provided by the literature extrapolated against these scenarios, we proposed research recommendations in Section 4 to help us remedy deficiencies in the state of our knowledge. This report and further work based upon these recommendations should prove beneficial in society's efforts to deal with the control, treatment, and disposal of hazardous wastes in our environment.

ABSTRACT

The state-of-the-art of available methods for predicting the effects of high chemical concentrations on the properties, processes, functions, cycles, and responses of terrestrial and aquatic ecosystems was reviewed. Environmental problems associated with high chemical concentrations can occur in soil and water at landfills; landfarms; spill sites; and abandoned chemical production, chemical use, chemical storage, and chemical disposal sites.

Considerable information is available on effects of trace chemical contaminants, such as pesticides, polychlorinated biphenyls, chlorinated hydrocarbons, and metal ions,in the respective ecosystems. Predictive techniques are becoming available to describe transport and transformation of such contaminants and, thus, their fate and distribution in certain components of the environment. High chemical contaminant concentrations are levels of application that are more easily expressed as percentage (i.e., 5% or greater) and cause major physical, chemical, or biological changes in the soil and water.

Present predictive methods and models that trace transport and transformation of chemical species are based on "natural" soil and water properties such as density, porosity, infiltration, permeability, viscosity, hydrophobicity, and diffusivity. When the chemical contaminant is present in high concentrations, then the assumption of "natural" soil and water properties is suspect. The major goal of this project was to assess the research needs that will address chemical contaminants present in high concentrations in terrestrial and aquatic ecosystems.

This report was submitted in fulfillment of Cooperative Agreement No. CR810480 by the University of Arkansas under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 13, 1982, to September 13, 1983, and work was completed as of September 13, 1983.

CONTENTS

Chapter		Page
	FOREWORD	iii
	PREFACE	iv
	ABSTRACT	v
	LIST OF FIGURES	vii
	LIST OF TABLES	viii
	ACKNOWLEDGEMENTS	ix
	CONCLUSIONS	x
1.0	INTRODUCTION	1
	1.1 System Definition	3
	1.2 Scope of Study	3
	1.3 Research Approach	6
2.0	LITERATURE REVIEW	10
	2.1 Chemical Properties	10
	2.1.1 Organic	10
	2.1.2 Inorganic	21
	2.2 Terrestrial Ecosystems	23
	2.2.1 Transport processes	24
	2.2.2 Transformation processes	28
	2.3 Aquatic Ecosystems	39
	2.3.1 Transport processes	39
	2.3.2 Transformation processes	43
3.0	SCENARIO OF HYPOTHETICAL CONTAMINANT CASES	44
	3.1 Terrestrial Ecosystems	45
	3.1.1 Binary solvent system	46
	3.1.2 Tertiary solvent system	56
	3.2 Aquatic Ecosystems	64
	3.2.1 Binary solvent system	64
	3.2.2 Tertiary solvent system	71
4.0	RESEARCH RECOMMENDATIONS	72
	4.1 Transport Processes	73
	4.1.1 Transport processes in saturated soils	73
	4.1.2 Transport processes in unsaturated soils	76
	4.1.3 Transport processes on the fluid side of earthen interfaces	77
	4.2 Equilibrium Processes	78
	4.2.1 Air-soil sorption processes	78
	4.2.2 Water-soil sorption processes	81
	4.3 Other Physico-Chemical Processes	83
	4.4 Transformation Processes	85
5.0	SUMMARY	90
6.0	REFERENCES	93
7.0	GLOSSARY	105
8.0	APPENDIX	109

LIST OF FIGURES

Figure		Page
1-1.	Matrix of chemical properties, transport and transformation processes, and soil and sediment properties which could influence the behavior of hazardous wastes.	7
2-1.	Three zones of sorption of chemicals onto soil from a leaky landfill.	18
2-2.	Five locations in the aquatic environment where chemical transport processes are important.	40
3-1.	EDC migration from a landfill.	49
3-2.	Benzene-phenol mixture migration from a landfill. . . .	57
3-3.	Creosote mixture in a streambed.	65

LIST OF TABLES

Table		Page
3-1	Physical and chemical properties of scenario substances.	47

ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of Ms. Nancy Miller and Ms. Anita Surin in the organization, literature search, and preparation of this report. They are also indebted to Mrs. Corinne Colpitts and Mr. Steve Dew for their help in conducting the computer search of the literature and to Ms. Connie Douthit for processing the manuscript.

CONCLUSIONS

Practical experience has demonstrated that high concentrations of chemical contaminants can have a very serious impact on terrestrial and aquatic ecosystems. The purpose of this report was to summarize the literature available on the environmental consequences of high concentrations of chemical contaminants in the soil, sediment, and aquatic environments. Scenarios of hypothetical contaminant cases in terrestrial and aquatic ecosystems for both binary and tertiary solvent systems indicated a very serious lack of information applicable to the cases. The vast majority of previous research has been conducted in aqueous systems at low chemical concentrations, and this is not the situation in a high concentration system.

The high chemical concentrations could vastly alter the transport and transformation processes, pathways, and kinetics because of their influence on the chemical, physical, and microbiological properties of the soil, sediment, and aquatic ecosystems.

Specific research topics in order of priority were proposed to reduce informational gaps which exist in our understanding of the impact of high concentrations of chemical contaminants on the environment. The research recommendations should help us to understand better the transport and transformation processes and, thus, be better able to deal with chemical contaminants in the environment.

1.0 INTRODUCTION

The impact of contamination of the environment by hazardous wastes at places such as Times Beach in Missouri and Love Canal in New York has received extensive popular press coverage (Fine, 1980; Sun, 1983). Public awareness of hazardous wastes has been greatly increased in recent years by such incidents, and the magnitude of the problem is increasing. The Office of Technology Assessment has estimated that the annual production of hazardous wastes in the United States approaches 250×10^6 metric tons (Norman, 1983). Much of the waste is relatively low hazard material such as fly ash from coal-burning power plants; however, the U.S. Environmental Protection Agency regulates disposal of approximately 40×10^6 metric tons per year of hazardous wastes of which some 80 percent is disposed of on land (Norman, 1983). In some instances contaminants enter the groundwater and pose human health hazards, and remedial actions are sometimes not feasible (Pye and Patrick, 1983).

The purposes of this report are to provide a state-of-the-art review of the impact of high chemical contaminant concentrations on terrestrial and aquatic ecosystems, to define informational gaps, and to develop research recommendations which provide data to better evaluate and manage contaminated systems.

The purpose of this project is to assess the state-of-the-art of available methods for predicting the effects of high concentrations of chemical contaminant on the properties, processes, functions, cycles, and responses of terrestrial and aquatic ecosystems. The safety, health, and welfare of the public and the environment in general can

be enhanced by increased knowledge of the behavior of these soil-water-chemical mixtures. As our increasing use and demand for chemicals interact with increasing population, encounters of the biota with those mixtures will multiply dramatically. Knowledge of the nature of these mixtures will enhance our ability to reduce the risk of exposure to toxic/hazardous substances by allowing more accurate prediction of behavior in the ecosystem and by supplying information which will assist in the design of treatment, storage, and/or disposal facilities (an aid to permit writers).

In this report, the terms hazardous waste, toxic substance, and chemical contaminant will be used according to the following definitions:

hazardous waste - dangerous discards generated from our highly industrialized, technologically based society; refers to any waste or combination of wastes that present or pose potential dangers to human health and safety or to living organisms in our environment; such wastes are lethal, non-degradable or may be biologically magnified, capable of promoting detrimental cumulative effects as well as short-term hazards; toxic chemicals, flammable, radioactive, explosive or biological in nature and take the form of solids, sludges, gases or liquids.

toxic substance - a poison; a substance that through its chemical action usually kills, injures, or impairs an organism.

chemical contaminant - a chemical substance that makes (water or soil) inferior or impure by admixture, makes unfit for use by the introduction of unwholesome or undesirable elements or compounds.

The results of this study will a) establish the magnitude of the problems associated with high chemical concentrations in uncontrolled sites, b) reveal the information gaps that exist concerning the behavior of the mixtures, and c) develop a set of recommendations for research needs.

1.1 System Definition

In this report high chemical concentration in the environment is taken to mean a level of single or joint chemical content in a phase (i.e., air, water, or soil) that constitutes $\geq$ 5 % (wt), or $\geq$ 50,000 ppm (wt) of the mixture. This is not an arbitrary definition for several reasons. At the 5% level, the volume basis of the concentration should include the quantity of the contaminant present or significant error results (Thibodeaux, 1979). At the 5% level, basic properties of the natural phases (i.e., air, water, and soil) begin to be influenced significantly by the presence of the foreign substance. For example, transport coefficients can not be assumed to be constant and independent of concentration at this level. High chemical concentrations occur in both the soil and/or water and involve environmental problems that include landfills, landfarms, and spill sites as well as abandoned and active chemical production, use, storage, and disposal sites.

1.2 Scope of Study

Present predictive methods and models that trace the movement, bioconcentration; partitioning; transport; and microbial, chemical, and photochemical degradation rates of chemical species are based upon "natural" soil and water properties such as density, porosity,

infiltration, permeability, viscosity, hydrophobicity, and diffusion. When the chemical contaminant is present in high concentrations, then the assumption of "natural" soil and water properties is suspect.

The following are some problem areas involving high chemical concentrations:

a. Landfills and chemical dumps.

A current definition of a landfill is a land disposal site employing an engineered method for disposing of solid waste on land in a manner that minimizes environmental hazards by spreading the solid waste in thin layers, compacting the solid waste to the smallest practical volume, and applying cover material at the end of each operating day. Methods have been developed to modify this conventional sanitary landfill to make it acceptable to receive hazardous materials. Taken together, these modifications result in a "chemical waste landfill." In general terms, such operations hope to provide complete long-term protection for the quality of surface and subsurface waters from hazardous wastes deposited therein and against hazards to public health and the environment.

The current problems involving high concentrations of hazardous waste from such land disposal sites are not overly concerned with the present generation of well-sited and well-constructed chemical waste landfills. However, the placement of bulk liquids, organic sludges, and organic solids do give cause for problems in operation that can involve high chemical concentrations in leachate and vapors. The majority of problems involve the past practices of co-disposal of chemical wastes in municipal solid waste landfills, the mixing of chemi-

cal wastes (including liquids) with garbage to form a non-flowing landfill "solid," the placement of sludges capable of creating a hydraulic head in landfill cells, and other expedient means for disposing of chemical wastes. In the latter category the most common is the chemical dump which involves the placement of solids and liquids on the ground, in natural depressions, and in hastily dug pits totally insufficient for their containment. Abandoned dump or storage sites also fall into the latter category.

b. Landfarms, contaminated land, and spill sites.

Surface soils have received quantities of waste of high chemical concentration applied to the surface and/or incorporated into the soil. Landfarming or landspreading is an operation involving the placement of sludges and aqueous wastes upon the soil surface. Spreading and frequent plowing plus the addition of nutrients for the active microbial culture are operating procedures. Contaminated land results from normal chemical processing operations and involves high levels of chemicals on or near the soil surface. This land contains substances which, when present in sufficient concentration, are likely to cause harm, directly or indirectly to man. Much of this land is on former industrial sites which were developed and left in a contaminated condition as a result of industrial processes. A recent international conference has highlighted the problems and reclamation operations involving contaminated land (Essex, 1983). The accidental spill of solids and liquids during rail and road transport also results in contaminated soil and high chemical concentrations.

c. Aquatic releases and spills.

High chemical concentrations can also become associated with the aquatic environment. Episodic spills of large quantities of sinker chemicals in river systems result in the bottom sediment being highly contaminated such as an incidence involving chloroform spilled into the Mississippi River (Thibodeaux, 1977). Long term releases such as the kepone (decachloroocta-hydro-1,3,4-metheno-2H-cyclobuta[cd]-pentalene-2-one) contamination of the James River (Orndorff and Colwell, 1980), and PCB's in the Hudson River (Horn et al., 1979) highlight this mode of contamination which results in high concentrations in the sediment.

1.3 Research Approach

The state-of-the-art review of the effects of high chemical contaminant concentration on terrestrial and aquatic ecosystems entailed the following activities:

1. The development of a matrix to systematize other research activities and assure that all variables were considered. The matrix (Fig. 1-1) consisted of soil and sediment properties, chemical properties, and various process variables. The matrix covered those factors which will influence the behavior of high concentrations of chemical contaminants in landfills, landfarms, spill sites, and in abandoned chemical production, use, storage, and disposal sites. A similar approach was used by Phillips and Nathwani (1977) to assess the land disposal of industrial wastes.

2. A literature search (national and international in scope) profile was formulated and included both computer and manual

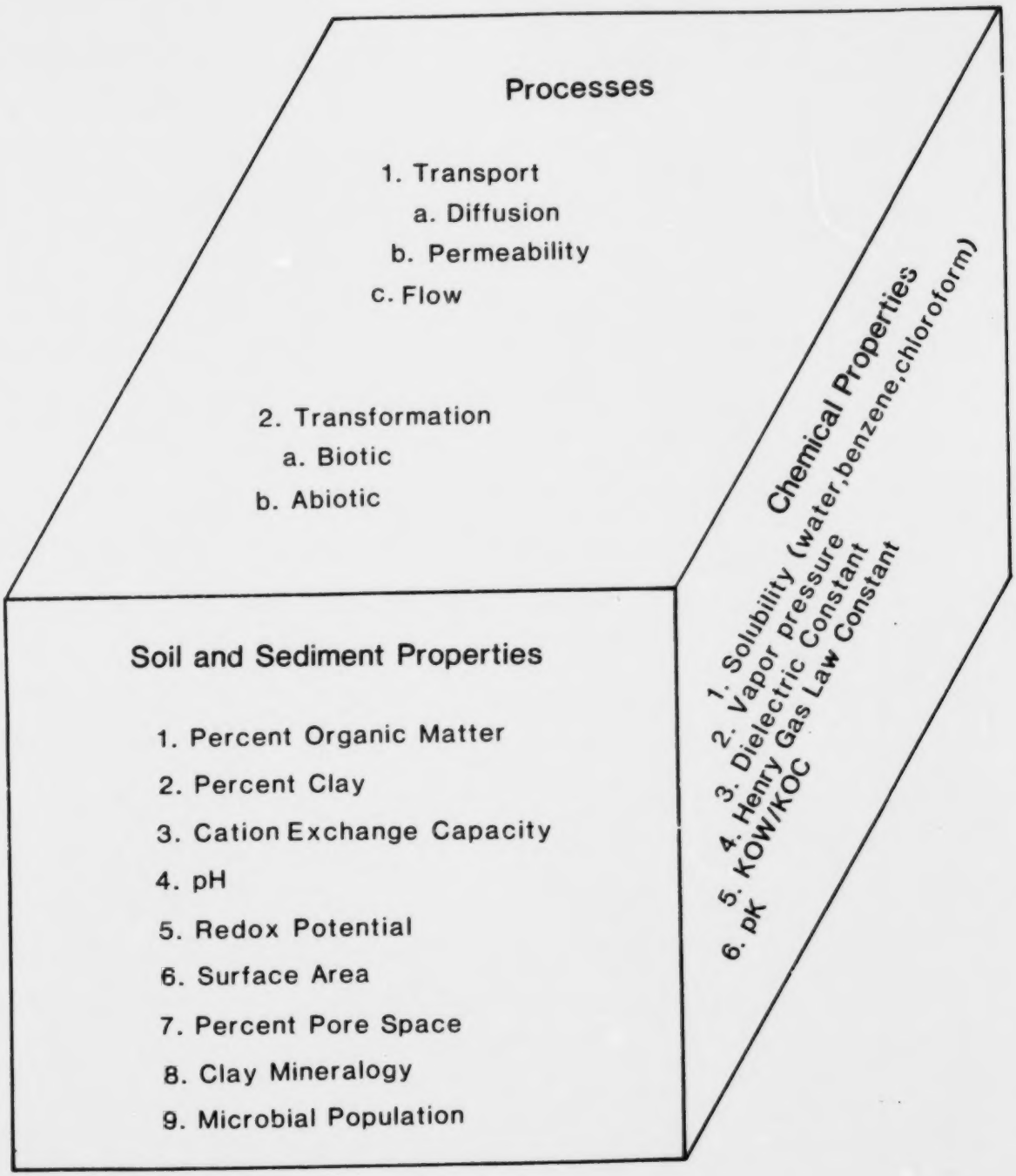


Figure 1-1

Matrix of chemical properties, transport and transformation processes, and soil and sediment properties which could influence the behavior of chemical wastes.

searches. Due to the current degree of high activity in the area of hazardous materials and the lag-time between abstracting and entry into computerized data bases, it was desirable to use manual search of journals, proceedings, and personal contacts originating within the last year to supplement the computer searches. It was assumed that all materials from 1981 and earlier had been abstracted and were available in the computer data bases.

The computer literature search was performed in conjunction with data bases available to the University of Arkansas Mullins Library and included: NTIS, AGRICOLA, BIOSIS PREVIEWS, CHEMICAL ABSTRACTS, SCISEARCH, ENVIROLINE, POLLUTION ABSTRACTS, ENVIRONMENTAL BIBLIOGRAPHY, WATER RESOURCES ABSTRACTS, and AQUALINE.

The computer search procedure included: a) the selection of key words based on the matrix, b) the use of Boolean logic to construct an ordering of the words, c) on-line search, d) typewriter output of titles, authors, and reference source details, e) review of titles by the Principal Investigators, and f) print out of selected abstracts. Based upon the content of the abstract, a copy of each pertinent journal article was studied.

3. A scenario analysis of hypothetical contaminant cases was also performed. One was a binary solvent system and the other a tertiary solvent system. The purpose of the scenario

analysis was to assess the impact of these waste solvents on soil and/or water properties/parameters such as acidity, hydrophobicity, thixotrophy, diffusivity, sorption, ion-exchange, porosity, permeability, biological activity, transformation reactions (chemical and biochemical) and their kinetics, volatilization, and mass transport processes (both mass flow and diffusion). The result of this exercise highlighted the extent to which the present state of knowledge in bacteriology, chemistry, engineering, physics, and soil science allows predictions involving the above property/parameters of the affected soil and water.

4. Based upon the results of the literature search and scenario analysis outcome, information gaps were identified.

5. Based upon the information gaps, a set of priority recommendations for needed future research (both field and laboratory) was developed.

2.0 LITERATURE REVIEW

This section summarizes the information available in the published literature that addresses the respective properties, processes, and transformations, with respect to high chemical concentrations in aquatic and terrestrial ecosystems. The literature on the subject is concerned mainly with trace contaminants in the environment; however, reference to that body of information will be covered only to the extent that it can be applied to high concentration situations.

2.1 Chemical Properties

2.1.1. Organic

a. Solubility. There is an abundance of data on the solubility of individual, pure organic chemicals in water at 25 C. This information is usually available in chemistry-related handbooks and in numerous other compiled sources (Dean, 1979; Reid et al., 1977; Perry and Chilton, 1973). The availability of data on the aqueous solubility of individual chemicals from mixtures of two or more components is lacking. The general effects and predictability of total organic content and dissolved salts of aqueous solutions on the solubility of individual chemicals are also lacking. This lack of information has important consequences with respect to leachates from landfills. The work by Chou et al. (1981) highlighted the effect of landfill leachates and dissolved salt content on the solubility of hexachlorocyclopentadiene. Some sources (e.g. Reid, Prausnitz, and Sherwood, 1977) describe physical chemistry techniques and compare various

algorithms of estimating solubilities of aqueous and non-aqueous mixtures. These techniques are in part based upon functional groups and chemical structure, i.e. structure activity relationships.

On the topics of liquid-liquid equilibria, partially miscible liquids, and solubilities of solids in liquids, the authors conclude that thermodynamics provides only a coarse but reliable framework. In many specific cases, the required information must be derived from basic physical and chemical theories and tested by laboratory research. The variety of mixtures encountered in the chemical industry is extremely large, and the set of reliable experimental data on mutual solubilities in aqueous and non-aqueous systems is extremely small in comparison (Perry and Chilton, 1973).

The disposal of liquid and solid wastes often results in mixtures consisting of two or more phases. The phases are typically aqueous and organic phases. Experimentally, under ordinary temperatures and pressures it is relatively simple to obtain the compositions of two coexisting liquid phases; as a result, the technical literature is rich in experimental results for a variety of binary and tertiary systems near 25 C and near atmospheric pressure. King (1969) outlines procedures for the Nernst's distribution law (i.e., partition coefficient approach) for non-reacting, association, dissociation, and chemical reaction systems. The emphasis is on the distribution of a substance between two phases (i.e., binary solvent). The Chemical

Engineer's Handbook (Perry and Chilton, 1973) contains a selected list of ternary systems that contains approximately 300 entries. These data are for high chemical concentrations. For example, there is an entry for the ternary system water-acetic acid-benzene. This system contains an aqueous phase with acetic acid and benzene in solution and an organic phase of acid and benzene with water in solution. The section entitled "Phase Equilibriums" should be consulted in Section 15 - Liquid Extraction of the Handbook (Perry and Chilton, 1973) as an entry to the literature for binary, ternary, quaternary, and other multicomponent systems.

Finding applicable equilibrium solubility data for a particular waste mixture is highly unlikely; however, data on closely related systems may be located, which are useful along with established thermodynamic methods (Reid, Prausnitz, and Sherwood, 1977).

b. Vapor pressure. An abundance of data and methods is available concerning vapor pressures of chemicals in the pure state. These data cover the range of low and high concentrations with respect to the air-phase and are available in raw form or correlated by the Clausius-Claperyon or Antoine equations. Lang's Handbook (Dean, 1979) is a typical source of such data.

Chemicals that exist in high concentrations in terrestrial and aquatic ecosystems are typically in an impure state. Most frequently, the chemical exists as a component of a mixture either with other chemicals or with water, soil, sludge, or a

combination of these phases. A complete review of vapor pressure information must include each mixture system separately.

The practice of collecting and disposing organic liquid wastes has resulted in the creation of mixtures. Mixing of similar and not so similar organic solvents, paint sludges, tank and still bottoms, semi-solid sludges, and other wastes is a means of consolidation and reducing storage capacity requirements. Fortunately, such mixtures are not unlike natural fossil hydrocarbon fluids, coal derived fluids, and mixed reaction products of the chemical process industries. The multicomponent nature and gas-liquid equilibrium relationships of such mixtures have been studied extensively over the past 60 years so that a considerable body of knowledge exists by which to predict individual partial pressures of specific chemical species in the mixture. Literature cited in Chapter 8 of The Properties of Gases and Liquids by Reid, Prausnitz, and Sherwood (1977) is representative of that literature.

The vapor pressure of organic chemical species dissolved in water is normally handled by a Henry's constant, particularly for dilute solutions. Phase Equilibrium in Mixtures by King (1969) presents information on this subject and cites applicable literature. Recent work has been aimed at verifying Henry's constant calculation techniques for miscible and immiscible dilute binary mixtures (Warner et al., 1980). Lack of data and model testing is apparent for vapor pressures with high chemical concentrations that result when water resides in contact with a multicomponent

liquid phase. A specific example for consideration would be the prediction of the partial pressures of benzene, furfural, carbon-tetrachloride, and a PCB above an aqueous solution which had been in contact with an organic phase consisting of equal portions of each chemical.

Several operations in the disposal of organic chemicals involve the intimate contact with the soil. For this system partial pressures of individual species are important. Disposal operations involve the dumping of organic chemicals into landfills and the placement and subsequent spreading of organic sludges, oily sludges, or wastewater treatment sludges onto land in the so-called land treatment operations. Other events of importance are the accidental spills of organic liquids and solids onto soil or terrestrial ecosystems and the placement of pesticides on or under the soil surface for agricultural pest control.

In all these situations soil water plays an important role. It appears that if sufficient soil water is present and dilute solutions exist, then Henry's constant can be used to obtain partial pressures for solution concentrations up to the solubility limit. Spencer, Farmer, and Jury (1982) in a recent review observed that the vapor pressures of lindane, DDT, and trifluralin dropped to very low values when the water content was decreased below that equivalent to approximately 1 molecular layer presumably by adsorption due to an increased competitive advantage. Significant differences in vapor density (or

pressure) occur for dieldrin when soil water is reduced from 3.94% to 2.1%.

This occurrence and the observations that the vapor emission rate from soils increases dramatically under certain conditions of soil moisture suggest that our knowledge of the equilibrium physical chemistry processes of dilute chemical soil mixtures in the range of unsaturated to "bone-dry" soil water conditions is lacking. Cupitt (1980) used the Brunauer, Emmett, and Teller (BET) modified Langmuir adsorption theory to estimate the vapor pressures of toxic chemicals adsorbed onto "bone-dry" aerosols. He gives no data to support the validity of the BET model. Bailey and White (1970) suggest that the same model can be used for pesticides on soils. However, the work of Jurinak and Volman (1957) on ethylene dibromide adsorption on dry soils suggests that this approach is reasonable for high concentration systems.

Various sludges generated by industrial operations and wastewater treatment operations contain waste materials that are potentially hazardous. Three general types of organic sludges or organic matter can be identified: 1) natural organic matter produced from normal soil processes such as biological decay products from biomass material consisting of grass, leaves, agricultural residues, and other organic material; 2) bio-sludges produced from microbial cultures of wastewater treatment plants such as activated sludge, anaerobic digesters, primary filtration, and others; and 3) oily/chemical sludges from petroleum, petrochemical, or organic chemical manufacturing operations which include

sources such as American Petroleum Institute (API) oil separators, tank bottoms, and still bottoms.

Partial pressures of selected chemicals from some of the chemical process sludges may be estimated by conventional techniques used in process design as outlined by Perry and Chilton (1973). A simplified verson of this design was employed by Thibodeaux and Hwang (1982) in modeling the air emission from a petroleum landfarming operation. The vapor pressure of the volatile species "dissolved" in the oily sludge can be estimated with Raoult's law. Raoult's law applies well if solute and solvent have no heat of mixing and no volume change on mixing. These "ideal solution" rules are likely valid for cases such as benzene in API sludge or in still bottom sludges; however, these specific equilibrium systems have little support data. For vapor pressures of volatiles above bio-sludges and natural organic matter "solvents," no studies have been found.

c. Chemical Partition Coefficient between Soil and Water (i.e., K_p, K_{ow}, K_{oc})

The partition coefficient, K_p, for trace chemicals between earthen solids, either soil or sediment, is defined as the ratio at equilibrium of the concentration on the solid to the concentration in water. In soils and sediments the adsorption of aromatic hydrocarbons and chlorinated hydrocarbons as expressed by K_p is directly related to the organic carbon content of the adsorbent. In such systems, it is convenient to use the term K_{oc} which is simply K_p divided by the organic carbon content of the

adsorbent. The K_{OC} has also been shown to be closely correlated to the octanol/water distribution coefficient or K_{OW} for several compounds (Karickhoff et al., 1979; Chiou, Porter, and Schmedding, 1983). A similar conclusion was reached by Brown and Flagg (1981) in their study of nine chloro-s-triazine and dinitroaniline compounds.

The partition coefficient will likely need to be generalized to include high chemical concentrations. It is unlikely that a simple ratio will suffice. The present generation of useful correlations covers a very narrow range of conditions that include organic chemicals in surface soils which have considerable organic matter content. These correlations are typified by the recent work of Chiou, Porter, and Schmedding (1983).

The spectrum of research scenarios for the adsorption (or solution) of chemicals onto (or into) soil systems needs to be broadened. The work of Anderson, Brown, and Green (1982) on the influence of adsorbed organic fluids on the change in permeability of clay soils highlights this need. Fig. 2-1 depicts a leaky landfill and shows three zones where the sorption of chemicals onto soil may be quite different. The zones are zone-1, leachate plume; zone-2, groundwater and leachate interaction; and zone-3, trace containment.

The first zone is characterized by high chemical concentrations and possibly additional liquid phases that overwhelm the subsoil adsorption capacity for the leaching constituents.

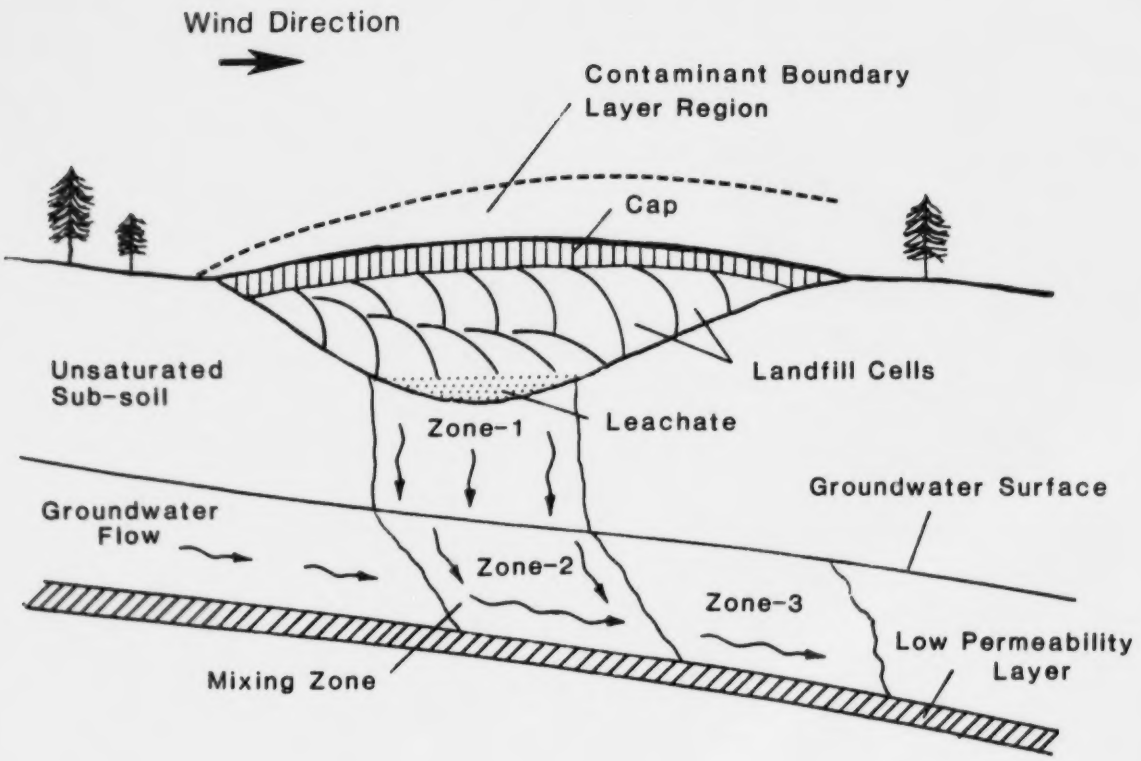


Figure 2-1

Three zones of sorption of chemicals onto soil from a leaky landfill.

For a given subsoil system the information currently available in the literature does not allow one to estimate the quantity of chemical adsorbed without performing simulation experiments. Adsorption is largely based upon the organic matter content of the soil, which may not exist for subsoil systems, or if it does, the high chemical concentration overwhelms the "solution" or solvent capacity of the organic matter. Recent research work involving the sorption of pesticides in the presence of co-solvents such as water-methanol and water acetone, in subsurface environments appears to be a realistic approach in extending the retardation factor concept to include such high concentration mixtures (Rao et al., 1983).

It is also possible that certain classes of organic chemicals such as phenolic compounds may undergo polymerization reactions as described by Wang et al. (1978a) and result in the formation of humic-like materials which have properties similar to soil organic matter (Martin et al., 1972). Should this occur, it would be possible to develop a synthetic soil horizon with increased "organic matter" levels which would more nearly approach the description of an A rather than a B horizon. This could result in increased adsorption of the chemical compound.

The second zone is characterized by a dilution process that occurs as the leachate plume meets and mixes with the passing groundwater stream. Two liquid phases may continue to exist in zone-2. Zone-3 is characterized by a secondary leachate plume that is created as the groundwater picks up and transports

constituents from zone-2 to points farther afield.

Spill sites and contaminated land introduce scenarios of high chemical concentrations related to sorption onto surface soils. Freeze and Cherry (1979) present the stages of migration of oil seeping from a surface source and define a residual oil saturation. This parameter is defined as a stable stage when an oil spill on a soil surface is held in a relatively immobile state in the pore spaces. Experiments in our laboratory (Altenbaumer et al., 1982) with the organic liquids, propanol, acetone, ethylene glycol, crude oil, and motor oil suggested that surface tension was the most important independent variable affecting the residual saturation. Residual saturation is the volume of liquid immobilized divided by the initial soil pore volume. Values ranged from 0.33 to 0.75, indicating that 33% to 75% of the available soil void volume was occupied by the liquids. The residual saturation for water was 0.26 for this soil which had 1.42% organic matter.

The above range of soil contaminant conditions, trace contaminants to concentrated leachates to pure fluids, is the state of many important hazardous substance problems for which adsorption equilibrium information is almost totally lacking. A comprehensive approach including theory and experiments along the lines of Dexter and Pavlou (1978) seems to be an appropriate first step. Incorporated into this approach are functional groups and chemical structure parameters which must be included in any comprehensive approach due to the varied nature of the

organic chemicals involved.

2.1.2 Inorganic

When a metal ion is introduced into an environment such as a waste disposal site, it can undergo numerous chemical and biochemical reactions. Only a few of the basic reactions will be presented in the following discussion, and cadmium will be used as a typical example of an inorganic, heavy metal, hazardous waste material.

Cadmium may exist as inorganic aqua complexes and the divalent cation, Cd^{+2}, in aqueous solution. It may also be adsorbed onto the clay or organic matter exchange complex which is important in reducing or preventing leaching of the metal. Cadmium may also exist in numerous other soluble inorganic and organic forms and in insoluble forms which are discussed in greater detail in the following section.

a. Solubility product. At high concentrations when the activity of an inorganic ion such as cadmium exceeds the solubility product of a given solid phase, then precipitation will occur. The solid phase will tend to buffer the concentration of the ion in solution. The situation is further complicated by the fact that attainment of equilibrium is not instantaneous and the solid phases are not pure, but vary in composition (Lindsay, 1972). In a pure system of a divalent cation and hydroxide anions, one possible equilibrium would involve

$$\underset{\text{(solid)}}{M(OH)_2} \rightleftharpoons M^{+2} + 2OH^-$$

The solubility product constant, K_{sp}, is given as $K_{sp} = [M^{+2}][OH^-]^2$. In a cadmium system, the K_{sp} for OH^-, CO_3^{-2}, S^{-2}, and PO_4^{-3} systems is 10^{-13}, 10^{-14}, 10^{-28}, 10^{-32}, respectively (Lisk, 1972). The data represent aqueous systems of the respective ions and do not involve any mixed ionic or non-aqueous systems which might be typical of hazardous disposal sites.

b. Chelates or Complexes. In addition to the various ionic species which may be present in an environmental system, generally a number of soluble metal chelates or complexes will also exist. The soluble organometallic chelates are important because they increase the solubility and, thus, the mobility and bioavailability of the metal. Norvell (1972) presented stability diagrams which compared the Cd^{+2} chelating ability of 11 common chelating agents in soil solution. The results indicated that DTPA was the most effective chelating agent at pH $\geq$ 7. At pH values typical of acid subsoils, none of the materials were effective chelating agents. In soil, sediment, or aquatic systems, the fulvic and humic acids are the naturally occurring chelating agents. In disposal sites, a complex mixture of organic compounds could be available for chelate formation, and subsequent movement in a nonaqueous environment could be a potential problem.

Chelation of trace metals such as cadmium is dependent upon the amount and type of organic compounds in the system, but metal ion speciation also depends upon the amounts of inorganic ligands such as phosphate and carbonate. Sposito and Mattigod (1979) developed a computer program called GEOCHEM to calculate trace

metal equilibria and the system has been valuable in assessing trace metal chemical reactions which occur in soil and water systems.

Avnimelech and Raveh (1982) reported that chelates were not adsorbed by soil, nor were they degraded under anaerobic conditions. These authors further pointed out the serious problem that could result if direct drainage of anaerobic leachates from a waste disposal site into a water system were to occur.

c. Biomethylation. Methylation of toxic metals by microorganisms plays a significant role in metal transport, and it may serve as a detoxification mechanism for the microbial population (Saxena and Howard, 1977). Methylcobalamin has been shown to transfer the methyl group to mercury which results in formation of monomethyl and dimethyl mercury in soils and sediments. Methylation also increases toxicity and/or the transportability. Due to solubility and volatility, the methylated materials are highly mobile in the environment. Other metals which are subject to methylation are arsenic, selenium, tellurium, lead, tin, and possibly cadmium.

2.2 Terrestrial Ecosystems

The literature review in this section covers occurrences of high chemical concentrations and their influence on processes near the air-soil interface and in the soil and subsoil layers down into the water table zone.

2.2.1. Transport processes

a. Saturated Soils. Wallace (1982) reviewed groundwater models with emphasis on application to the petroleum industry. He concludes that solute (contaminant) transport models are in an early stage of development compared to flow models; consequently, the use of transport models is more limited. For the movement of many wastes, the cause-effect relationships, especially those involving physical-chemical behavior, are only partially understood. In theory some complex reactions (e.g., oxidation-reduction and precipitation-dissolution) can be addressed; in practice chemical reactions are either ignored or approximated by very simple equations. Some of the technical difficulties still to be overcome relate to situations where quality and quantity of flow cannot be handled separately. Where relatively high contaminant concentrations affect the flow pattern, e.g., where density differences affect the movement and mixing of the groundwater flow, coupling of the flow and quality models must occur (see Fig. 2-1).

Results of a recent symposium and workshop focusing on hazardous waste management also highlighted the lack of information on contaminant dispersion in ground-water systems (Worm, Dantin, and Seals, 1981). There is a problem in using conventional computation techniques to predict the directions of motions of contaminants into the aquifer through spills or injection. The motion of dispersion is due to changes in the relative viscosity of the liquids, density of the liquids, adsorptive pro-

cesses within the liquid, and refractive properties of the aquifer material. The interrelationship of the fields of motion upon one another are not presently known.

Anderson, Brown, and Green (1982) demonstrated in the laboratory that organic fluids can substantially increase the permeability of compacted clay soils. Chemicals selected represent four classes of organic fluids and include acetic acid, aniline, methanol, acetone, ethylene glycol, heptane, and xylene. Clays included montmorillonite, illite, and kaolinite. Results of this work indicate the need to test premeability of prospective clay liners using the high chemical concentration of leachate to which they will be exposed.

b. Unsaturated Soils and Vadose Zones. The transport of chemicals of high concentration in the vapor phase has received some consideration. Applications involve mathematical models and have been concerned with the movement of such substances from landfills and landfarms. The work of Alzaydi et al. (1978), McOmber et al. (1982), and Moore et al. (1979) is mainly concerned with the methane-air mixtures between 5% and 15% with respect to explosion hazards in construction facilities near landfills. Gas generated in landfills exhibits high concentrations and total pressures just greater than atmospheric. Thus, small total pressure gradients and high partial pressure gradients exist. Combined transport mechanisms must be used because diffusional and pressure flows are competitive. Thibodeaux (1981) and Thibodeaux, Springer, and Riley (1982) developed models for the

vapor phase transport of benzene, chloroform, vinyl chloride and Aroclor 1248 from a landfill cell to the soil surface. Three of the chemicals are at extremely high concentrations. Three transport mechanisms were identified as being important - diffusion, bio-gas purge, and barometric pressure pumping (e.g. the movement of soil gas by changes in atmospheric pressure) - in moving the hazardous vapors to the soil surface. The verification of important aspects of this model is presently underway (Springer and Thibodeaux, 1982).

The accidental spill of organic chemicals onto soil surfaces or the placement of waste-containing volatile chemicals onto soil surfaces for so-called "land treatment" operations creates situations involving complex transport mechanisms. Thibodeaux and Hwang (1982) present an oversimplified model for the emission of chemical vapors from high concentration sources at the soil surface. This model neglects soil-water gradients, thermal gradients, and capillary gradients. The lack of consideration of these gradients may severely limit the utility of the model to real-world applications.

The transport of radioactive waste constituents in unsaturated zones was considered by Winograd (1981). He makes reference to the fact that conclusions reached apply equally to chemical toxic wastes in trenches. The idea of waste storage in these zones has received only peripheral attention to date for several reasons: the paucity of hydrogeologic, soil physics, geochemical, tectonic, and other data for the unsaturated zone

where indeed few direct measurements of the flux of vadose water have ever been attempted at depths of a few meters, and the uncertainty on how retardation factors, yet to be measured for unsaturated flow conditions, will compare with those reported for saturated flow.

c. Air Boundary Layer above Soil. For chemicals that exist in pure form or as constituents of a solid or liquid waste mixture on the soil surface, the transport through the successive boundary layers (i.e., sub-layer, buffer zone, and turbulent zone) provides the only resistance for volatile transport to the air. Information on the transport of high chemical concentrations in the air boundary layer is undergoing investigation from the point of view of the catastrophic release, spread, and dispersion of cryogenic gases such as liquified natural gas and liquified petroleum gas (Havens, 1982). This work involves dense clouds formed by cold gases. Very little information in the literature is associated with ambient ground sources such as chemicals from solid waste dumps and liquid pools. The modeling work by Springer (1979) with hydrazine spilled on airport runways involves high chemical concentrations; however, conditions of dispersion were chosen that overlook the effect of the presence of a dense gas on stability and the need for wind to transport and disperse the dense chemical vapor. A recent work by Thibodeaux and Scott (1984) alluded to the problem areas with transport rate prediction in the air boundary layer even for trace contaminants. In the field, environmental transport pro-

cess are complicated by the coexistence of mechanical and thermal turbulence. Due to these physical effects, field-observed mass-transfer coefficients will display a high degree of apparent random fluctuations. The verification of the combined mechanical/thermal model under field conditions presents a formidable task. Once verification has been performed for bare soil and short grass conditions, the effects of crop canopy must be addressed.

2.2.2 Transformation processes

Transformation processes involve the conversion of the parent compound to any different chemical compound(s). The processes may result in the complete degradation of the parent compound to such end products as carbon dioxide, water, and inorganic halide ions in the case of certain chlorinated organic compounds. The transformation could result in the production of large molecular weight polymers for certain reactive phenolic materials or a series of daughter products present in different proportions. Numerous other fates could result depending upon the material in question, the environmental conditions, and a host of other parameters.

In this discussion, transformation processes will be treated as biotic, which involves a biological system, or abiotic, which is strictly a physical or chemical reaction. In certain situations one of the processes may be dominant and, therefore, is the major degradation pathway. However, it should not be overlooked that in many real world situations, the two processes may work in concert to determine the ultimate fate of many chemical materials.

a. Biotic transformations

Microbial degradation is an extremely important process in the transformation of numerous organic chemicals. The bacteria, actinomycetes, and fungi in soil, water, and sediment are the decomposers of many organic materials. Environmental conditions such as optimum temperature, pH, moisture, aeration, inorganic nutrient levels, concentration of the organic material, and the population level of the microbial community all influence the rate of degradation for many organic chemicals. In general, maximum degradation will occur at neutral pH values, temperatures in the 30 C range, soil moisture levels of 0.25 to 0.35 bars, aerobic conditions, adequate levels of N, P, and S, and concentrations of the organic substrate below levels toxic to the microorganisms. For aromatic compounds, the general degradation pathway has been summarized by Pal et al. (1977) and involves (i) oxidation of side chains, (ii) fission of the benzene ring, and (iii) metabolism of short chain acids to yield carbon dioxide, water, energy, and microbial biomass.

There are many exceptions to the general guidelines, and in most cases each chemical or mixture of chemicals must be considered on a case-by-case basis. As would be expected, the half-lives of many of the organic materials of interest have been shown to range from a few hours to many years in the environment.

Recently, Edgehill and Finn (1983) demonstrated that the direct inoculation of acclimated pentachlorophenol-utilizing

Arthrobacter cells to a contaminated soil increased the disappearance of the chemical by a factor of 10. The half-life of pentachlorophenol was reduced from 14 days to approximately 1 day in both laboratory and field studies. The data also indicated the importance of mixing the soil during inoculation to increase the overall efficiency of degradation in the field study. Raymond et al. (1976) also noted the importance of mixing the soil in their study of oil degradation in soil. Such mixing would be possible in surface application of hazardous wastes, but in a landfill environment, a lack of mixing would result in decreased degradation rates.

The influence of concentration of organic chemicals on their biodegradation rate has numerous implications. Much of the degradation research conducted on pesticides has been at levels of 1 to 10 kg/ha rates. Boethling and Alexander (1979) concluded that laboratory tests of decomposition at concentrations other than what was found in the natural system may not be valid and they showed that low concentrations may be important in limiting biodegradation in natural waters. At the other end of the concentration spectrum, extremely high levels of organic and inorganic chemicals are antimicrobial (Buddin, 1914) and degradation can proceed only when the level decreases to some level tolerated by the microbial population which degrades the material in question.

In reviewing the effects of pesticides on microorganisms in soil and water, Parr (1974) noted that high concentrations of

chlorinated hydrocarbon insecticides could exert an inhibitory influence on the soil microbial population. In general, the inhibitory influence was eventually overcome and the microbial population and activity returned to pretreatment levels. Martin (1972) conducted extensive research on the impact of soil fungicides and fumigants on soil microorganisms. Since fungicides and fumigants are applied to the soil as antimicrobial agents, a dramatic impact on the microbial population is not unexpected. Using the fumigants chloropicrin, carbon disulfide, and D-D (dichloropropene-dichloropropane mixture), Martin (1972) reported that there was a dramatic initial reduction in microbial numbers which was followed by a large proliferation of microbes. He noted that the greater the initial reduction in microbial numbers, the greater the subsequent peak in population. With time periods of several months, the population returned to a level comparable to the untreated soil. He also stated that the nitrifying bacteria were especially sensitive to the soil fumigants.

The influence of high rates of 20 pesticides on microbial numbers and activity was reported by Stojanovic et al. (1972). Soil amended with a pesticide rate of 11.2 metric tons/ha exhibited a reduction in bacterial and fungal numbers following 56 days of incubation for such compounds as dieldrin and DDT. Ou et al. (1978) evaluated the response of the soil microbial population to high 2,4-D (2,4-dichlorophenoxyacetic acid) applications. In a sandy loam soil amended with 20,000 ppm 2,4-D, the fungal,

actinomycete, and bacterial populations were significantly decreased over an 11-week study.

Recent work by Paris et al. (1981) has demonstrated the second-order kinetics aspect of three pesticides which undergo hydrolytic degradation. Using natural waters and low pesticide concentrations, the researchers showed that the degradation rate was proportional to both bacterial and xenobiotic concentrations.

It is also possible that the microbial population will alter a given chemical such as DDT and yet the responsible microbes do not increase in number nor is the compound utilized at a rate sufficient to sustain microbial growth. In other words, the microorganisms grow on one substrate while degrading a second material. Such a degradation scheme has been termed cometabolism and may be extremely important as the first step in degradation of recalcitrant molecules (Alexander, 1981).

As one specific example, let us consider the microbial degradation of the compound phenol. Early research by Buddin (1914) showed that phenol concentrations of 0.94% to 9.4% (weight basis) in soil "kept the soil life in an inactive condition" during a 75-day incubation study. At concentrations of $\leq$ 0.09%, the soil bacterial population exhibited substantial increases in response to the added carbon. Varga and Neujahr (1970) isolated phenol degrading microorganisms from soil and indicated that aerobic degradation proceeded by formation of catechol. In the presence of oxygen, the catechol ring was cleaved to yield either succinate plus acetate or pyruvate plus acetaldehyde. In either

case the materials readily enter established metabolic pathways in the microbes and are used as carbon and energy sources.

Under strictly anaerobic conditions, phenol is biodegraded to methane and carbon dioxide with 70% of the carbon converted to gas during a 29-day study (Healy and Young, 1979). In recent studies, Scott et al. (1982 and 1983) reported that as the phenol concentration increased from 10^{-5} to 10^{-2} M, the lag phase increased from $\leq$ 5 h to $\geq$ 23 h. These results demonstrate the antimicrobial properties of phenol. At concentrations of 10^{-9} to 10^{-6} M phenol, the half-life was from 2.3 to 3.7 h in two soils studied, an indication of the relative ease of degradation at sub-toxic concentrations.

Fannin et al. (1981) showed increased phenol degradation when the bacterial inoculant was increased, and they reported a significant influence on phenol degradation related to the type of growth medium used. At high phenol concentrations, the addition of supplemental nitrogen, phosphorus, and sulfur would be expected to enhance the assimilative capacity of the soil, but little work has been conducted on the topic (Overcash and Pal, 1979).

One case where the biotic-abiotic transformations appear to overlap is that of bioconcentration. A limited number of studies have shown that microorganisms in soil could serve as an active sorption site of organic chemicals and can concentrate the chemicals. Grimes and Morrison (1975) investigated the bioconcentration of chlorinated hydrocarbon insecticides by thirteen

soil bacteria. They observed bioaccumulation of various insecticides with all the bacteria studied, and found that the degree of bioconcentration was inversely proportional to the water solubilities of the insecticides. Once sorption had occurred, the insecticides were not easily desorbed from the bacterial cells. They suggested that the pesticides were sorbed into the lipid material of cells, and that desorption may not occur even after cells died and lysed.

Paris et al. (1977) conducted bioconcentration studies of toxaphene by soil microorganisms. They observed that cultures of autoclaved fungi, bacteria, and algae sorbed just as much toxaphene as viable cells of the same treatments and, thus, suggested that bioconcentration is not an active process. Percich and Lockwood (1978) found that mycelia of six living actinomycete species accumulated between 900 to 4,300 µg atrazine/g dry mycelium. Autoclaved mycelia sorbed 100 µg atrazine/g dry mycelium during the same time. Greater variability was observed with fungi. Living fungal mycelia bioaccumulated between 20 to 6,600 µg atrazine/g dry mycelium.

b. Abiotic transformations

Adsorption plays a pivotal role determining the fate of many organic and inorganic materials in the environment (Weber and Weed, 1974). As the given hazardous material is partitioned between the solid and liquid, solid and gaseous, or liquid and gaseous phases, the specific concentration available for degradation or transport is determined. As with microbial degradation,

a vast amount of literature has been published related to pesticide adsorption by soils and sediments in aqueous systems, but far fewer data are available which relate to high concentrations. Also, as was the case with microbial degradation of pesticides, the adsorption literature was developed from the perspective of low concentrations of organic materials in aqueous systems. LaFleur (1973) studied the adsorption of the herbicide fluometuron (3-(m-trifluoromethylphenyl)1,1-dimethylurea) by soil in solvent systems of water, ethanol, acetonitrile, dichloromethane, and n-hexane. He noted that adsorption of fluometuron by a Cecil B2t soil (subsoil with a clay texture) in a dichloromethane system was linear over the concentration range of 10 to 10,000 mol/kg. As the number of adsorption sites became limiting, the partitioning exhibited a curvilinear response. Thus, adsorption at lower concentrations could be described by Freundlich isotherms, but adsorption at higher concentrations was best described by Langmuir isotherms.

Parathion adsorption by clays and lake sediments was increased by addition of the nonionic organic dye, rhodamine B, decreased by addition of phenol, or not influenced by methylene blue addition (Wang et al., 1972). This was one of the few studies to use a multicomponent solution in the adsorption system. Mills and Biggar (1969) also conducted early studies in nonaqueous systems using BHC (1,2,3,4,5,6-hexachlorocyclohexane). They used a Ca-Staten peaty muck to study adsorption of BHC from both aqueous and hexane solutions. The Freundlich K values at 20

C were 330 and 0.8 for the aqueous and hexane solvents, respectively. It should be noted that, in using organic solvent systems which extract soil organic matter, it is likely that the amount of adsorption could be altered as well as the mechanism of adsorption.

Limited work has been conducted in nonaqueous systems, but it has shown that adsorption in organic solvent - soil or sediment systems is not comparable to pesticide adsorption at low concentrations. However, factors such as percent clay, cation exchange capacity, and organic matter levels appear to play important roles in adsorption.

A second abiotic transformation is chemical degradation which may include such reactions as hydrolysis, oxidation, and reduction. Under defined conditions, each of the three reactions have been demonstrated.

Armstrong and Konrad (1974) have reviewed nonbiological degradation of pesticides and noted that considerable evidence has been published to show that sorption-catalyzed chemical hydrolysis plays a major role in degradation of the chloro-_s_-triazines. Sorption catalyzed hydrolysis has also been shown to be important in degradation of organophosphate insecticides. Walker and Stojanovic (1973) reported that malathion (_S_-(1,2-dicarbethoxyethyl)-_O_-_O_-dimethyldithiophosphate) was susceptible to chemical degradation. The degradation was greatest in a clay soil, and hydrolysis was most rapid in the alkaline pH range. Another herbicide, dalapon or 2,2-dichloropropionate, was shown

to undergo hydrolysis in aqueous solution to yield pyruvate and hydrochloric acid. At a dalapon concentration of 2.4 M, the hydrolysis resulted in a 5.4% loss of the parent compound after 14 days at 23 C (Tanaka and Wien, 1973).

Trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N,dipropyl-p-toluidine) degradation has been shown to be a reduction reaction which was accelerated by anaerobic conditions (Parr and Smith, 1973). Subsequent research by Willis et al. (1974) showed that maximum trifluralin degradation in soil occurred only when the Eh decreased below a critical range between +150 and +50 mV.

Another example of a reduction reaction in soil was reported by Wahid et al. (1980). The insecticide parathion (O,O-diethyl O,p nitrophenyl phosphorothioate) was shown to be reduced to aminoparathion in as little as 5 sec in prereduced soils. The reduction appeared to be mediated by heat-labile substances, possibly enzymes, produced by soil anaerobisis.

The third abiotic transformation process which has been described is photodegradation which involves chemical reactions resulting from electromagnetic radiation. In general, only chemical compounds which absorb the sun's UV radiation above 285 nm are expected to undergo photodecomposition (Armstrong and Konard, 1974). In the case of soils, only materials applied to or which are transported to the soil surface are expected to be subject to photodecomposition and such reactions have been demonstrated for numerous pesticides and have been reviewed by Plimmer (1970). One specific example for monuron (3-(p-chlorophenyl)-1,1-dimethyl-

urea) was reported by Crosby and Tang (1969). They show that photodecomposition of monuron in an aqueous system exposed to sunlight followed a stepwise photo-oxidation and demethylation of the N-methyl groups, hydroxylation of the aromatic portion of the molecule, and subsequent polymerization. Crosby and Wong (1977) studied the photodegradation of TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) on inert surfaces, plants, and soils. They reported almost total disappearance of TCDD when exposed to 6 h of natural sunlight if the dioxin was dissolved in a light-transmitting film and an organic hydrogen-donor such as a solvent was present. These results could have important implications related to photodegradation of chemical contaminants in binary solvent systems on soil surfaces.

An additional abiotic transformation process which has been studied involves catalytic polymerization of phenolic compounds on clay surfaces. Wang et al. (1978a, 1978b) tested three clay minerals and solutions of various phenolic compounds and demonstrated that oxidative polymerization occurred which resulted in the formation of dark colored organomineral complexes. The catalytic activity was in the order illite (2:2) > montmorillonite (2:1) > kaolinite (1:1) and was also related to the Fe and Al content of the materials tested. The polymeric material resembled soil humic and fulvic acid with regard to several chemical properties. Subsequent work showed that, as the pH of the phenolic solution was increased to 8.5 in the presence of illite, the polymerization rate increased due to increased

free radical formation and greater autooxidation. Solomon et al. (1968) also reported the role of clay minerals in oxidation by showing that benzidine was changed to benzidine blue at aluminum atoms exposed at the edges of the clay. Pinnavaia et al. (1974) used the mineral hectorite and the aromatic compound toluene to demonstrate the formation of a toluene radical cation and subsequent polymer formation.

2.3 Aquatic Ecosystems

2.3.1. Transport processes

The literature does not contain very much information on the study of transport processes in aquatic ecosystems with emphasis on high chemical concentrations. Incidences related to transportation accidents and inadvertent releases from manufacturing sites account for the placement of high concentrations of lighter-than-water (floaters) and heavier-than-water (sinkers) chemical substances in aquatic ecosystems. Specifically, some of these incidences are oil slicks on river and lakes from tanker accidents, bottom contamination involving chloroform from a river barge accident, bottom contamination involving carbon tetrachloride from an inadvertent episodic release to a river, and bottom contamination involving creosote waste discharged continuously over a long period of time. Fig. 2-2 depicts five locations in the aquatic environment where chemical transport processes are important. The labeled locations are a) bottom sediment, b) bottom water, c) water column, d) surface water, and e) boundary layer.

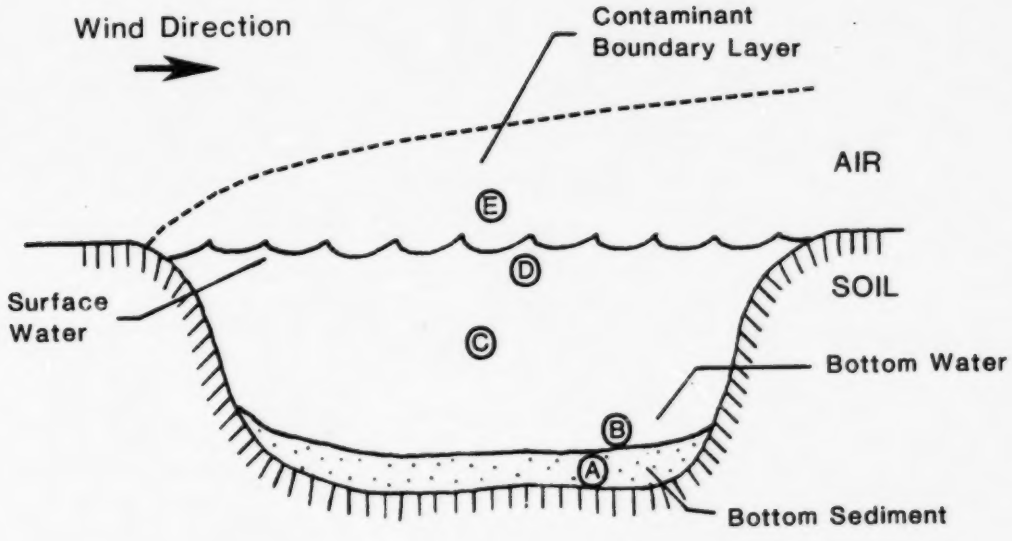


Figure 2-2

Five locations in the aquatic environment where transport processes are important.

Very little is known about transport in the stream-bed sediment region. This zone of the aquatic ecosystem is the recipient of wastes of high chemical concentration, particularly near and on manufacturing sites. Sinker chemicals, those with a density greater than water, enter streams and go immediately to the bottom. Once on the bottom a pool, consisting of a separate phase, forms in the low depression. Under such conditions, an apparent physical inflow of an organic chemical substance into the porous bottom sediment can occur because of the increased static gradient of the dense chemical, attraction for the natural organic material in the bed sediment, and coverage by the natural sediment transport processes. A specific case is the downward perculation of ethylene dichloride from a plant site stream bed to a position 50 feet below the surface. No technical information is available to describe the transport mechanisms of chemicals involved in such occurrences. Ashworth (1982) performed some laboratory simulation experiments with carbon tetrachloride on sand, coarse gravel, and compacted mud. No penetration was observed in the sand, but some did occur in the gravel and in the mud.

Some aspects of the behavior and transport of chemicals on the stream bed surface have been studied and reported. Thibodeaux (1977) and Christy and Thibodeaux (1982) reported on studies of the spill of soluble, high density, immiscible chemicals on water. Qualitative aspects of the behavior of this class of sinker chemicals was studied in aquatic system simulators.

Mechanisms observed were jet break-up, rapid settling of pure chemical droplets through the water column, and coalescence into globs and pools on the bottom. Quantitative aspects, including the bottom water transport coefficient in model flowing streams, were measured and correlated to stream parameters of water velocity, water depth, sand wave depth and sand grain size (Thibodeaux, Chang, and Lewis, 1980). The important physical parameters for transport rates in the bottom water of unstratified lakes and surface impoundments are wind speed, water depth, and water fetch (i.e. the distance wind travels over water) (Thibodeaux and Becker, 1982). Wafers of pure benzoic acid placed on the bottom surface were used to measure transport rates.

Theoretically, high chemical concentration layers, made up of an aqueous solution or made of a pure organic phase of density near unity, can form near the thermocline of lakes or the pycnocline in the ocean. Sewage and industrial effluents have been observed in stratified waterbodies occupying positions in the water column near the pycnocline. Information relating to chemical transport processes of such layers was not found.

Oil and "floater" chemical slicks on the surface of water is a well-documented phenomena, and there is much information in the literature concerning spreading, dispersion, and transport processes. In some respects the air boundary layer above the surface of water is not unlike that above the soil. This is particularly true under low wind conditions when wave action is

at a minimum. The work by Havens (1982) involving the catastropic release, spread, and dispersion of cryogenic gases also involves the air boundary layer above water. This work and related ongoing research by the U.S. Coast Guard and the British Coast Guard research organizations comprise the literature available on this condition (Havens, 1982).

2.3.2 Transformation processes

Many of the biotic and abiotic transformation processes applicable to an aquatic ecosystem have been previously discussed in section 2.2.2. However, the sediment with the highly reducing conditions below the water-sediment interface presents a different environment where aerobic degradation will not occur, and thus, the degradation rate will generally be much slower.

3.0 SCENARIO OF HYPOTHETICAL CONTAMINANT CASES

A scenario analysis of two hypothetical contaminant cases was undertaken. One involved a binary solvent system (aqueous and non-polar organic) and the other a tertiary solvent system. Each of these solvent systems was applied to a terrestrial and an aquatic high chemical concentration contamination scenario, respectively.

Given that the systems are known, the purpose of the scenario analysis is to assess the impact of these solvents on such soil and/or water properties/parameters as acidity, hydrophobicity, thixotrophy, diffusivity, sorption, ion-exchange, porosity, permeability, biological activity, transformation reactions (chemical and biochemical), and their kinetics, volatilization, and mass-transport processes (both mass flow and diffusion). The result of this exercise will highlight to what extent the present state of knowledge in bacteriology, chemistry, engineering, physics, and soil science allows prediction of the above property/parameter/process of the affected soil and water.

This project appears to collect data to substantiate the obvious. Concentrations of chemicals in the range to be investigated will certainly have catastrophic effects on the characteristics of any ecosystem. The relevant questions are how can such concentrations be kept from spreading to other ecosystems and how can they be best controlled within or dispelled from the ecosystem. Although this project will contribute very little toward that goal, a prerequisite to successful disposal of hazardous wastes is to assess the state-of-the-art of general knowledge about chemicals in the environment, particularly from the point of view of predictability in the ecosystems.

True predictability, based on first principles, implies that we understand and can quantify all the relevant properties/parameters/processes. Questions of whether to spread, clean-up, or leave in-place, can then be addressed, and results of the simulation models can be applied with confidence. In this light, a scenario analysis can give some indication of the capability for prediction.

3.1 Terrestrial Ecosystems

Scenario: Metal drums of organic liquids were placed in a sanitary landfill approximately 20 years ago. The waste was co-disposed with municipal waste consisting mostly of waste paper and other cellulosic material. The cell was constructed in such a way that the waste was buried under 6 m of overfill (subsoil) and other wastes. The landfill was capped with 50 cm of clay and 50 cm of surface soil. Evidence has accumulated to indicate that the waste has been released from the drums and exists as free liquid in the cell. Some rainwater has entered the cell so that a two-phase liquid system is assumed to exist in the bottom of the cell. The bottom of the cell is 5 m above groundwater.

This terrestrial ecosystem contamination scenario provides the framework for considering the fate of chemicals moving upward to the atmosphere, downward to the groundwater, and in the lateral direction. The hypothetic binary solvent system consists of water and 1,2-dichloroethane. The tertiary solvent system consists of water, benzene, and phenol.

3.1.1. Binary solvent system

The fate of 1,2-dichloroethane (EDC) in the environment with respect to conditions of low concentrations has been addressed (Callahan, 1979). As is typical of current fate analyses, the specific topics of interest are photolysis, oxidation, reduction, hydrolysis, volatilization, sorption, bioaccumulation, and biodegradation. The implied scenario in these conventional fate studies calls for extremely dilute solutions with the source of chemical contaminant located some distance removed from the study site (i.e., far-field). In contrast, the present scenario calls for high concentrations with the source of chemical contaminant located at or very near the study site (i.e., near-field). Table 3-1 lists pertinent physical/chemical properties of EDC and other substances.

A study of the properties of pure EDC indicates that, when it is released from the metal drum, the pure liquid, with specific gravity of 1.253, will have a tendency to percolate downward. Gravitational acceleration will force the liquid through the other (porous) waste materials and onto the bottom of the landfill cell. If water has accumulated in the bottom section, EDC will continue to move down and eventually come to a temporary halt. The continual arrival of EDC from the corroding drums will form a pool of nearly pure liquid in the lower portions of the cell and under the water layer.

The migration downward does not stop here but continues. Being 25.3% heavier than water the apparent "hydraulic" head can

Table 3-1. Physical and chemical properties of scenario substances (Callahan, 1979; Dean, 1979; Perry and Chilton, 1973).

	benzene	1,2-dichloro-ethane	phenol	naphtha-lene	penta-chlorophenol
Formula	C_6H_6	$C_2H_4Cl_2$	C_6H_5OH	$C_{10}H_8$	C_6Cl_5OH
Molecular weight	78.12	98.98	94.11	128.16	66.35
Melting point (C)	5.5	-35.4	40.9	80.6	190.0
Boiling point (C)	80.1	83.5	182.0	218.0	10.0
Vapor pressure (torr) at T C	95.2/25	61/20	0.529/20	0.0492/20	0.00011/20
Solubility in water, (mg/L) at T C	1780/25	8690/20	93,000/25	34.4/25	14/20
Log (octanol/water) partition coeffi-cient	--	1.48	1.46	3.37	5.01
State at 15 C and 1 atm.	liquid	liquid	solid/ liquid	solid	solid
Specific gravity at T C	0.879/20	1.253/20	1.058/41	1.145/20	1.98/15
Liquid surface tension, (N/m) at T C	0.0289/20	0.0322/20	0.0365/55	0.02/80	--
Liquid water interfacial tension (N/m) at T C	0.035/20	0.03/25	0.02/42	0.05/80	--
Latent heat of vapor-ization, (J/kg)	3.94E5	3.2E5	3.0E5	3.38E5	--

force fluid through the liner (if it exists) and into the vadose zone of the subsoil. The EDC will enter the groundwater and continue to move until it encounters a rock formation or strata with very low permeability. At this point coalescence again occurs and pure pockets of EDC form on top of these strata. Figure 3-1 maps the gross features of the downward percolation of EDC.

a. Chemical properties and concentrations

Solubility - Mutual solubilities (e.g., EDC in water and water in EDC) can likely be obtained from the literature. Models are available to estimate mutual solubilities as a function of temperature.

Vapor pressure - The vapor pressure of EDC has been measured and models are available to estimate the vapor pressure as a function of temperature.

Sorption on cellulosic material - As EDC percolates through the waste in the lower cell, it will be sorbed by the cellulose in such materials as the waste paper and vegetable cuttings. Neither the extent of this sorption in g EDC/g cellulose nor the vapor pressure of EDC in the resulting mixture can be estimated at present.

b. Soil properties

Porosity - The soil porosity that results after a wave of pure EDC has passed cannot be estimated at this time. It is possible that EDC may change the porosity of the soil matrix. A general indication could be made if the extent of sorption

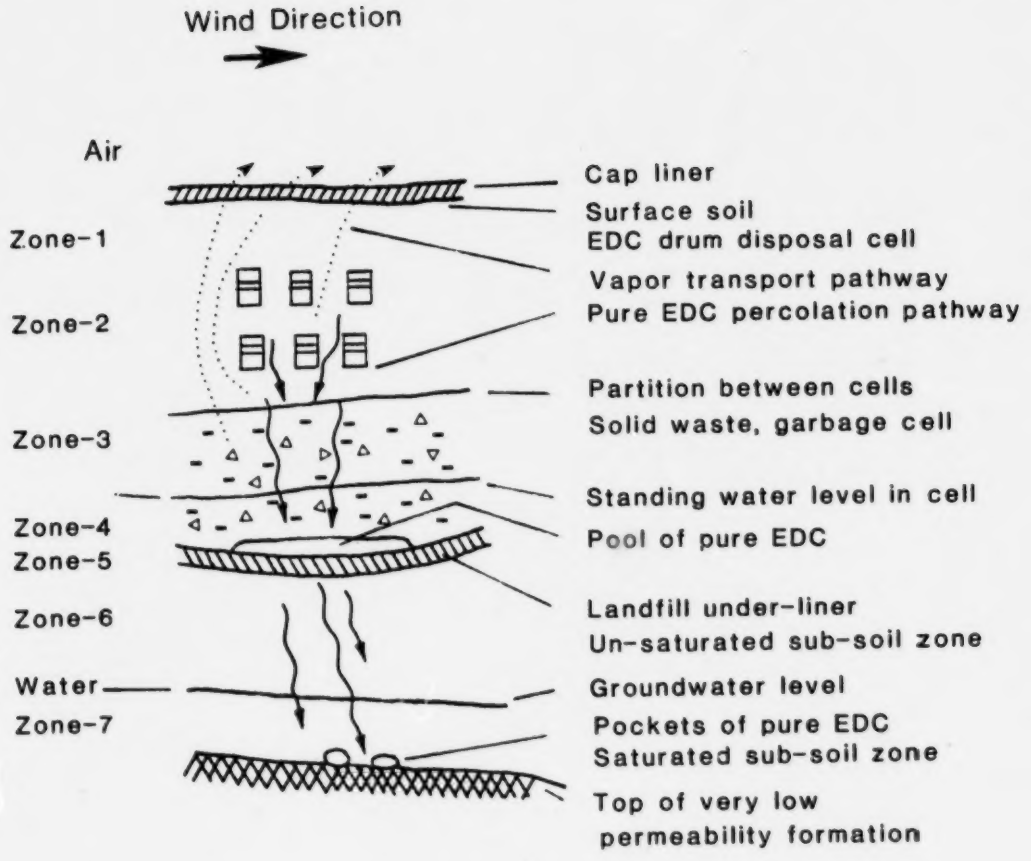


Figure 3-1

EDC migration from a landfill.

were known.

Sorption - The normal partition coefficient is not applicable where a surface soil or subsoil is exposed to a pure fluid phase such as EDC. The traditional partition coefficient is defined as the concentration of contaminant on the soil divided by its concentration in the soil-water. In this case there is no soil-water but instead there is pure EDC. A few measurements of sorption on soils with pure substances have been made. Jurinak and Volman (1957) sorbed ethylene dibromide onto soil from the vapor phase and reported a value of up to 0.12 g/100 g. Sims and Overcash (1983) report values for the adsorption of benzene on smectite (Wyoming montmorillonite) as a function of organophillic cation and water content. Competition between water and the aromatic molecules has the most obvious effect on the adsorption of benzene. Benzene adsorbed (no water) ranged fom 13.8 to 22.6 g/100 g. No general principles are available, other than to assume a Langmuir adsorption and compute the quantity for one monolayer coverage based on knowing the surface area.

Ion-exchange - not applicable.

Solvation - The possible alteration of the clay fractions of the soil due to irreversible sorption of EDC at interlayers of crystal structure is not predictable at this time.

Organic matter - Since the EDC is in contact with soil material that is either a subsoil (B horizon) or parent material (C horizon) the amount of organic matter solubilized

would be low since the level of soil organic matter is low. However, it would be expected that a portion of the organic material in the codisposed waste could be extracted and, moving with the EDC, could facilitate mobility of metal chelates if they were present in the waste.

Microbial Population - The high EDC concentration would most likely result in the death of the limited microbial population present in the lower part of the landfill. The microbial population normally present in the subsoil would be very low. Only when the concentration decreased to subtoxic levels would the microbial population be expected to reestablish following introduction of microbes from non-fumigated areas.

c. Transport properties

Diffusivity - Molecular diffusion is an important transport process for EDC in the air and liquid filled spaces of the landfill. Molecular diffusivity estimation techniques of chemical species in gas and liquid mixtures are well developed, particularly for substances with low molecular weight (Reid, Prausnitz, and Sherwood, 1977). Reliable estimates involving large complex molecules such as dieldrin (1,2,3,4, 10,10-hexachloro-exo-6,7-epoxy-1,4,4a,5,6,7,8,8a-octa-hydro-1,4-endo-exo-5,8-dimethanonaphthalene), heptachlor (1,4,5,6, 7,8,8-heptahcloro-3a,4,7,7a-tetrahydro-4,7-methanoindene), 2,3,7,8-TCDD, and others are crudely developed and untested. A recent field study by Glotfelty, Taylor and Zoller (1983)

points out the uncertainty of molecular properties on diffusivity and dispersion into the atmosphere. For EDC in both the gas-filled pore spaces and the liquid-filled (i.e., water, EDC mixture) pore spaces, the current estimating methods should yield reliable values.

Permeability - The permeability of landfill generated liquids through soil liners is receiving considerable research attention (Acar et al., 1984; Brown and Anderson, 1980). The permeability of soils to chemical vapors is receiving very little attention (Springer and Thibodeaux, 1982). The permeability of soil to pure EDC, EDC-water mixture, and EDC vapor is unknown, and no methods are available to obtain an estimate.

Capillary rise - Liquids are forced to the soil surface or nearer to the soil surface by capillary rise. A granular material (sand or grit with acceptably low silt content) is necessary to allow the drainage of the overlying soil and also to reduce to an acceptable level the capillary movement of water-soluble pollutants up the soil column (Cairney, 1982). The role of capillary rise in moving EDC to the surface cannot be assessed at this time.

Viscosity - The viscosity is an important transport property due to the dependence of permeability on fluid viscosity. There are reliable methods for estimating viscosities of mixtures such as EDC and water.

Model Concepts - The models currently proposed for the pre-

diction of transport of pollutants are inadequate for high chemical concentration situations because they were developed for situations where the pollutant is present in concentrations in the ppm or ppb range. This includes transport in both the fluid-water phase and the vapor-air phases. The current models arise from studies with dilute solutions. For water-diluted pollutant transport it is possible to piggyback the pollutant model on the hydraulic (Darcy's law) aquifer model because the presence of the pollutant interferes insignificantly with hydraulics. The retardation factor approach (Letey and Farmer, 1974), another feature of dilute solutions models, is completely inadequate if a pure organic phase is present in the aquifer. The reliability of present-day models to predict the fate of EDC in zone 7 of Fig. 3-1 is extremely poor. Vapor phase transport models for zones 1, 2, 3, and 6 are also at a very crude state of development. Current models are inadequate for making reliable predictions of the movement of EDC from the landfill source to the air or water ecosystems.

d. Transformation processes

Microbial degradation of the EDC and the remaining cellulosic material in the landfill would most likely be an extremely slow process. In the landfill environment anaerobic conditions would result in fermentation metabolic pathways which are well defined for such materials as cellulose. However, a deficiency of nitrogen, phosphorus, and sulfur

would drastically reduce microbial activity and, thereby retard degradation. Other factors which would inhibit cellulose decomposition would include low soil temperatures, acid pH levels, and an inherently low microbial population.

Van Engers (1978) studied the anaerobic mineralization of an organic leachate from a waste disposal site in Holland. He reported that highly reduced conditions existed under the disposal site where redox potentials were less than -120 mV. The low redox values were conducive to anaerobic microbial activity, and he demonstrated that both sulfate reduction and methane production occurred with the quantity of methane plus carbon dioxide produced equal to 10 µl/g wet soil/h in a laboratory experiment.

The presence of high levels of EDC would most likely result in an antimicrobial influence and thus eliminate the already highly stressed microbial population. As the concentration of EDC decreased to subtoxic levels by the various transport avenues, the population could be reestablished, but activity levels would be very low. In general, the microbes will utilize the most available carbon substrate first which should translate as a preferential utilization of cellulose within the limits of nutrient deficiency and other stresses imposed. No data were located which were directly applicable to the given circumstances.

Bioconcentration would not be expected to be of significance in the system.

Abiotic transformations in the system are even more difficult to predict. Sorption on the cellulosic waste would be an important consideration, but data are not currently available to allow assessment of its magnitude. Adsorption related to soil organic matter or cation exchange would not be expected to be significant. Chemical degradation for a stable compound like EDC would not be expected; however, no data are available to support such a statement. Sorption-catalyzed hydrolysis of atrazine in an acid environment has been demonstrated to be very important (Armstrong and Konrad, 1974). Hydrolysis of 2,2-dichloropropionate at high concentrations has also been shown to occur (Tanaka and Wien, 1973).

With the current information, it is not possible to evaluate the importance of photodegradation of the EDC vapor over the landfill. Polymerization reactions would be unlikely.

In general terms, transformation reactions would be very limited in the hypothesized environment. However, the basis for such a statement is mainly supposition, and few data are available which are directly applicable to the case in point. The vast majority of the decomposition studies conducted have been under conditions to optimize microbial activity, and the system defined here represents the other end of the spectrum.

3.1.2. Tertiary solvent system

It will be assumed that benzene and phenol are present in the bottom of the landfill cell in proportions of 5% benzene, 5% phenol and 90% (weight) water. A study of the properties of the chemicals in Table 3-1 suggests a behavior pattern different from that of EDC. Although a two-phase system, consisting of organic and aqueous, will likely exist, the organic phase will float since the combined density will be less than unity. Fig. 3-2 shows the expected migration pathways.

The organic liquid mixture percolates through zone 2 and 3 and halts at the standing water level in zone 4. As long as water is present in the bottom of the cell to float the organic phase it will not contact the liner. Water moving through will dissolve some of the benzene and phenol from the organic layer. This leachate can then move through the bottom liner and toward the groundwater. Once arriving at the groundwater, a floating, low density leachate plume will form and ride atop the groundwater aquifer. Other transport processes are occurring and will be considered in detail below.

a. Chemical properties and concentrations

Solubility - Mutual solubilities of the three component system in the aqueous and organic phases can likely be estimated using existing methods. The maximum concentrations of benzene and phenol in the zone 4 water will be roughly approximated by the solubilities in Table 3-1.

Vapor pressure - The partial pressures of benzene and phenol

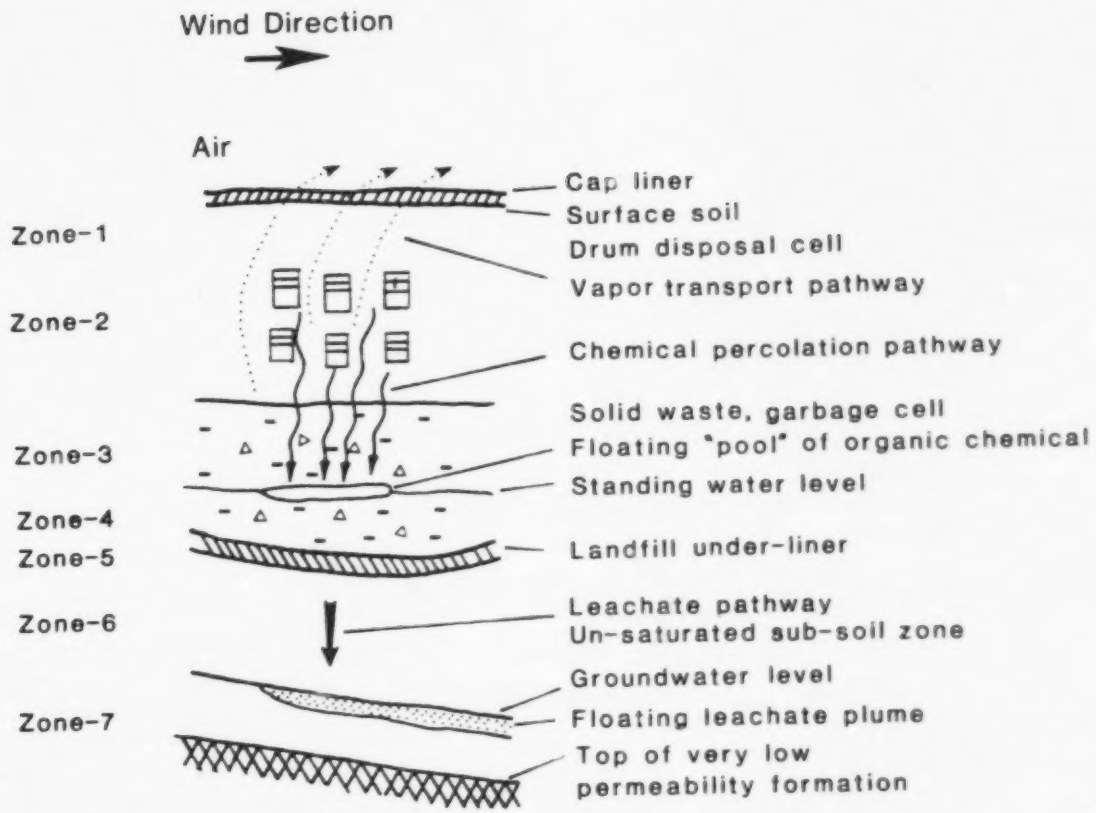


Figure 3-2

Benzene-phenol mixture migration from a landfill.

associated with the organic and aqueous phases can likely be estimated using existing methods. The partial pressures of the two organics can roughly be approximated by Raoult's law, although better procedures using activity coefficients are readily available.

Sorption on cellulosic material - As the organic phase percolates through other landfill materials, fractions will be sorbed. Just as with EDC in the binary solvent, a "trail" of contaminated waste solid/cellulosic material will be left behind as the benzene/phenol mixture moves downward from cell-to-cell. The extent and nature of this sorption process and the residual vapor pressures cannot be estimated at present.

Porosity - The soil porosity that results after a wave of a benzene/phenol mixture has passed cannot be estimated at this time. A general indication could be made if the extent of sorption were known.

Sorption - The normal partition coefficient is not applicable where a surface soil or subsoil is exposed to a pure fluid phase. The traditional partition coefficient is defined as the concentration of the pollutant on the soil divided by its concentration in the soil-water. A few measurements of sorption on soils with pure substances have been made. Jurinak and Volman (1957) sorbed ethylene dibromide onto soil from the vapor phase and reported a value of up to 0.12 g/100 g. Sims and Overcash (1983) report values for the adsorption of

benzene on smectite (Wyoming montmorillonite) as a function of organophillic cation and water content. Competition between water and the aromatic molecules has the most obvious effect on the adsorption of benzene. Benzene adsorbed (no water) ranged fom 13.8 to 22.6 g/100 g. No general principles are available, other than to assume a Langmuir adsorption and compute the quantity for one monolayer coverage based on knowing the surface area.

It should be noted that benzene sorption on organo-modified surfaces due to the presence of the organophillic cations may be similar to sorption on organic matter.

Ion-exchange - not applicable.

Solvation - The possible alteration of the clay fractions of the soil due to irreversible sorption of the organic compounds at interlayers of crystal structure is not predictable at this time.

Organic Matter - Since the benzene/phenol is in contact with soil material that is either a subsoil (B horizon) or parent material (C horizon), the amount of organic matter solubilized would be low since the level of soil organic matter is low. However, it would be expected that a portion of organic material in the codisposed waste could be extracted and, moving with the organic material, could facilitate mobility of metal chelates if they were present in the waste.

Microbial Population - The high organic chemical concentration would most likely result in the death of the

limited microbial population present in the lower part of the landfill. Only when the concentration decreased to subtoxic levels would the microbial population be expected to reestablish following introduction of microbes from non-fumigated areas.

c. Transport properties

Diffusivity - Molecular diffusion is an important transport process for benzene/phenol in the air and liquid filled spaces of the landfill. Molecular diffusivity estimation techniques of chemical species in gas and liquid mixtures are well developed, particularly for substances with low molecular weight. Reliable estimates involving large complex molecules such as dieldrin, heptachlor, 2,3,7,8-TCDD, and others are crudely developed and untested. A recent field study by Glotfelty, Taylor and Zoller (1983) points out the uncertainty of molecular properties on diffusivity and dispersion into the atmosphere. For benzene/phenol in both the gas-filled pore spaces and the liquid-filled (i.e., water, mixture) pore spaces, the current estimating methods should yield reliable values.

Permeability - The area of permeability of landfill generated liquids is receiving considerable research attention. The permeability of soils to chemical vapors is receiving very little attention (Springer and Thibodeaux, 1982). The permeability of soil to the benzene/phenol mixture, benzene/phenol-water mixture, and benzene/phenol vapor is unknown and

no methods are available to obtain an estimate.

Capillary rise - Liquids are forced to the soil surface or nearer to the soil surface by capillary rise. A granular material (sand or grit with acceptably low silt content) is necessary to allow the drainage of the overlying soil and also to reduce to an acceptable level the capillary movement of water-soluble pollutants up the soil column (Cairney, 1982). The role of capillary rise in moving the benzene/phenol mixture to the surface cannot be assessed at this time.

Viscosity - The viscosity is an important transport property due to the dependence of permeability on fluid viscosity. There are reliable methods for estimating viscosities of mixtures such as benzene/phenol and water.

Model Concepts - The models currently proposed for the prediction of transport of pollutants are inadequate for high chemical concentration situations because they were developed for situations where the pollutant is present in concentrations in the ppm or ppb range. This includes transport in both the fluid-water phase and the vapor-air phases. The current models arise from studies with dilute solutions. For water-diluted pollutant transport it is possible to piggy-back the pollutant model on the hydraulic (Darcy's law) aquifer model because the presence of the pollutant interferes insignificantly with hydraulics. The retardation factor approach, another feature of dilute solu-

tions models, is completely inadequate if a pure organic phase is present in the aquifer. The reliability of present-day models to predict the fate of the benzene/phenol mixture in zone 7 of Fig. 3-2 is extremely poor. Vapor phase transport models for zones 1, 2, 3, and 6 are also at a very crude state of development. Current models are adequate for making reliable predictions of the movement of benzene/phenol mixture from the landfill source to the air or water ecosystems.

c. Transport properties

Model concepts - In general the same comments apply as made for the binary solvent. For this particular scenario the current generation of groundwater pollutant transport models cannot handle: a) in situ leaching of components from the floating organic layer atop the standing water in zone 4; b) the dispersion and displacement behavior of the floating leachate plume that rides atop groundwater in zone 7.

d. Transformation processes

Microbial degradation of phenol at high concentrations would not occur because phenol is a potent antimicrobial agent (Buddin, 1914). As the concentration decreased to levels suitable for microbial activity, degradation under anaerobic conditions could occur given suitable environmental conditions and microbial population levels to result in the formation of methane (Healy and Young, 1979). If aerobic conditions existed at low phenol concentrations, degradation

would be rapid (Scott et al., 1983).

Benzene degradation would be limited by the lack of oxygen which would be necessary for the initial hydroxylation reaction and, thus, given the additional environmental stresses, would most likely be resistant to degradation.

Cellulose would most likely be the preferred substrate by any microbial population that did become established as was the case in the previous situation. Bioconcentration would not be an important factor.

Sorption of phenol has been studied at levels of 10^{-2} M by Scott et al. (1982) and was shown to be very low and related to organic matter levels in soil. However, soil adsorption would not be expected to play a major role in retention of phenol nor benzene.

If the phenol or benzene was oxidized to catechol under partially aerobic conditions, then it is possible that clay surface catalyzed polymerization of the material would occur (Wang et al., 1978a, 1978b). The polymerization would result in the formation of a dark colored complex material which would have some properties similar to soil organic matter and would be resistant to further degradation.

Other abiotic transformations would be expected to be limited in importance. Again, it should be stated that few data exist which apply directly to the defined system, but the above represents a plausible scenario of events all of which need further research data to validate.

3.2 Aquatic Ecosystems

Scenario: Due to the existence and operation of a creosote plant over a 20-year period, a nearby stream has received excessive waste sludge discharges. It appears that the streambed sediment for approximately 16 kilometers (10 miles) downstream is heavily contaminated with creosote sludge. Levels of up to 15% creosote have been measured in the bottom sediment. The stream has a very slow rate of flow (South Louisiana bayou) and the layer of contaminated sediment is roughly 20 cm deep. Creosote odors can be detected coming from the surface of the water at times of atmospheric inversions and low wind speed. Creosote is an oily liquid obtained from the destructive distillation of wood-tar. It will be assumed that the make-up of the waste is 5% naphthalene (NPH), 5% pentachlorophenol (PCP) and 5% of mixed organic material with properties similar to those of NPH and PCP. Fig. 3-3 shows general features of the contamination scenario.

This aquatic ecosystem contamination scenario provides the framework for considering the movement of chemicals upward to and through the water column to the atmosphere and downward to the groundwater. The binary solvent system will consist of water and naphthalene. The tertiary solvent system will consist of water, naphthalene, and pentachlorophenol.

3.2.1. Binary solvent system

The summary of fate data for NPH with respect to conditions of low concentrations has been addressed (Callahan, 1979). As is typical of current fate analysis, the specific topics of interest are photolysis, oxidation, hydrolysis, volatilization,

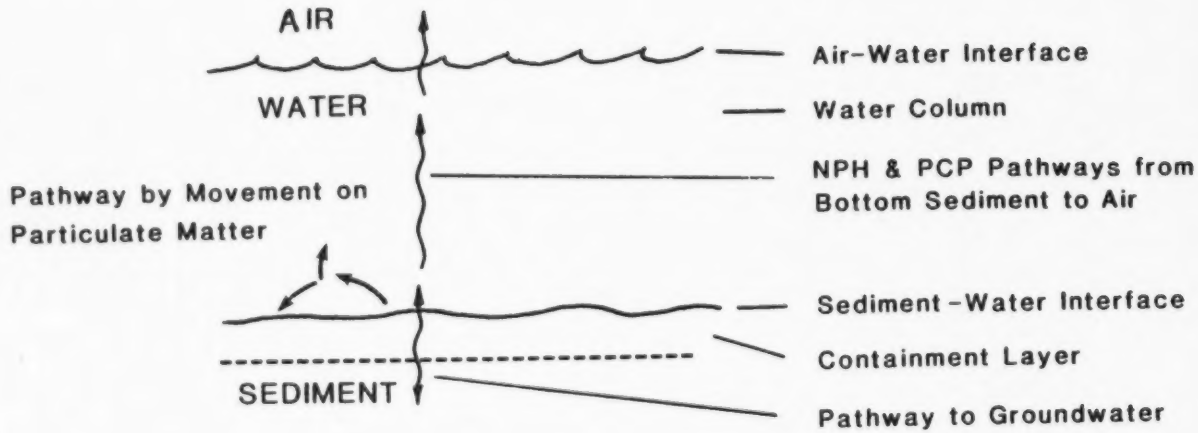


Figure 3-3

Creosote Mixture in a Streambed.

sorption, bioaccumulation, and biodegradation. The implied scenario in these conventional fate studies calls for extremely dilute solutions and far-field existence of the chemical. In contrast, the present scenario calls for high concentrations and near-field existence. Table 3-1 lists pertinent physical/chemical properties of NPH and PCP.

A review of the properties of NPH in Table 3-1 suggests some behavioral aspects. Naphthalene is a solid at the stream bottom-sediment temperature, and due to its density it will not float to the surface in bulk but will remain in place. The solubility in water is low but finite so that dissolution is a likely mode for transport from the sediment. Fig. 3-3 indicates that, once NPH leaves the sediment, it can enter the water column and then the air, and it can also enter the groundwater.

a. Chemical properties and concentration

Solubility - Mutual solubilities (e.g., NPH in water and water in NPH) can likely be obtained according to the literature. Models are available to estimate the solubility of pure NPH in water as a function of temperature.

Vapor pressure - The vapor pressure of NPH has been measured, and models are available to estimate the vapor pressure as a function of temperature.

Sorption on sediment material - Naphthalene readily adsorbs onto the sediment. Its association here is likely with the clay organic matter fines. The dilute solution calculated K_{oc} is 600 which suggests the sediment will attract and hold

a sizable fraction of NPH compared to the pore-water. Since correlations for K_{OC} are typically related to solubility, molecular weight, and melting point and are based upon data obtained under dilute solution conditions, it is doubtful that such correlations are applicable to sediment which contains 50,000 mg/kg of NPH and another 50,000 mg/kg of other organic material. Since pure NPH is present, the use of a K_{OC} is highly doubtful.

b. Water and sediment properties

Porosity - The effect of 50,000 mg/kg of NPH upon the porosity of the natural bottom sediment is unknown. In effect, this is 5% of the mass of the on-bottom material so that it is a dominant constituent.

Sorption - see sorption on sediment material section in part a. above.

Ion-exchange - Its role in this situation is likely not important.

Solvation - Since NPH is a solid, it is unlikely that components of the soil will be affected. The solubility of NPH in pore-water is fairly low, and no effect from NPH is expected at this low level, but the NPH is 5% of the sediment phase and much uncertainty exists on solvation processes.

c. Transport properties

Diffusivity - Molecular diffusion is an important transport process for NPH in the air, water, and liquid-filled pore spaces of the bottom sediment. Current available

estimating techniques should be reliable for the molecular diffusivity of NPH in air and water. For exceptions see section 3.1.1c.

Permeability - The gross features of permeability in bottom sediment is fairly well understood. This statement is more applicable to lake ecosystems than to river ecosystems mainly because of the lack of a substantial water movement in the lake and the uniformity of the sediment. The spatial variation in the permeability of the various upper layers in river bottom sediment is unknown for the most part. The bulk of the NPH is located in these upper layers. Due to sediment transport and bottom sand-wave forms, the upper layers of bottom sediment can enjoy a relatively high trickle-flow of water. Lower layers are more fully protected from the action of the flowing water and are usually more dense. Since permeability controls water movement in this region its importance with respect to chemical transport is dominant in particular for high concentrations of chemical in this region. At this time it is not possible to estimate the permeability of the NPH-contaminated sediment layer.

Viscosity - The viscosity of water may be affected slightly by the presence of NPH in solution. This is not thought to be an important consideration.

Transport phenomena in sediment - Diffusion transport of ions and some small organic molecules in ocean bottom sediment has received considerable attention. It appears that the pheno-

mena of hindered diffusion, as described by the retardation factor, is applicable to transport of organics such as NPH in bottom sediment provided the solution is dilute. Whether or not the retardation factor approach is appropriate at high concentrations is a question that needs to be investigated. The question, as pointed out in previous sections, revolves around the appropriate model concepts for adsorption onto the sediment phase.

The transport phenomena in the upper sediment layer are complicated because the process is not entirely controlled by diffusion. This layer is highly permeable, and significant water flow occurs so that convective transport is present. The relative roles of both convective and diffusive transport in the upper layers of sediment in river ecosystems is in a crude state of development. There is no clear means of estimating NPH transport out of the 20-cm contaminated layer.

Transport phenomena in the water column - As the chemical leaves the sediment in the upward direction, it does so by dissolution and by bed scour processes. The dissolution involves molecular transport through the water-side boundary layer followed by transport through the water column (both stratified and non-stratified conditions) and then through the air-water interface. A few studies have been conducted on chemical transport in these various zones but none with high chemical concentrations. Transport across the air-water interface region seems to be well understood, and many data

and models are available to quantify these transport parameters. The scour-settling-resuspension transport processes seem to be in a very crude state of development. Measurement has been attempted, but the level of development is very low. Detailed observations and studies involving high chemical concentrations are needed. High chemical concentrations, particular chemicals with high solubility, can cause stratification of a water column (not unlike thermal stratification of lakes) that can inhibit transport. There is no information on this aspect in aquatic ecosystems. In summary, the transport phenomena of NPH from the sediment water interface upward in the water column are not understood to such an extent that reliable predictions can be made.

Transport phenomena to groundwater - In general the phenomena involved here are identical to those in transport to groundwater covered in section 3.1.1.c. Since the solubility of NPH is essentially in the dilute range, prediction of the rate of movement downward can be performed within the range of reliability of existing groundwater transport models (Enfield et al., 1980).

d. Transformation processes

Microbial degradation of NPH under aerobic conditions proceeds by hydroxylation and subsequent ring cleavage. As in the previous examples, high NPH concentration and limiting conditions for microbial activity would suggest a slow degradation rate of the material.

3.2.2 Tertiary solvent system

This system consists of water, naphthalene, and pentachlorophenol. A study of the properties of the chemicals in Table 3-1 suggests no behavior grossly different from those of the binary solvent system.

4.0 RESEARCH RECOMMENDATIONS

The preceding section makes obvious informational gaps that exist in our understanding of the impact of high concentrations of hazardous wastes on the environment. The vast majority of earlier research was conducted in aqueous systems at low chemical concentrations, and the present work is concerned with high chemical concentrations in systems that include non-aqueous conditions.

At a given point in time and space, we can, for the most part, determine how much concentration of a substance is initially deposited into a terrestrial or an aquatic medium. The gaps in present-day data occur in relation to our knowledge of transport through the medium and throughout the ecosystem and transformation processes that alter the original substance. Understanding transport and transformation is complexed by the myriad variables which can exist in the medium and the ecosystem and by differences in the contaminants which can result from mixed deposits where multiple contaminants may interact. The impact of high waste concentrations on transport and transformation processes relate to 1) physical properties of the porous medium, 2) chemical properties of the porous medium, and 3) microbiological properties of the system.

Consequently, our research recommendations are proposed to bridge the gaps in information to date and to compile data on which to base calculations, predictions, and more specific research investigations in the future. The following recommendations are categorized under 1) transport processes in saturated soils, unsaturated soils, the fluid side of earthen interfaces; 2) equilibrium processes in air-soil sorp-

tion or water-soil sorption; 3) other physico-chemical processes; and 4) transformation by microbial degradation, abiotic reactions, photochemical processes, and behavior of organometallic complexes. These categories provide the order for the discussions which follow on research recommendations. The order of priority for those recommendations can be found in the Section 5.0, Summary, page 90.

4.1 Transport Processes

4.1.1 Transport processes in saturated soils

Research Recommendations

- °Laboratory simulation of leachate migration processes for high chemical concentrations
- °Model reformulation based upon the observed mechanisms to account for the density stratification and the presence of two phases

Many features of chemical transport processes in saturated (with water) soil below landfills and hazardous waste sites are poorly understood. The scenario in this report was based upon field observations at a number of landfills and abandoned waste sites and delineated three saturated zones: zone 1-leachate plume, zone 2-groundwater and leachate interaction, and zone 3-trace contaminant. Zone 1 is characterized by high chemical concentrations, and possibly additional liquid phases, that essentially overwhelm the subsoil adsorption capacity for the leaching constituents. Zone 2 is characterized by a dilution process that occurs as the leachate plume meets and mixes with the groundwater. Two liquid phases may continue to exist in zone 2. Zone 3 is characterized by a secondary leachate plume that is

created as the groundwater picks up and transports constituents from zone 2 to points farther afield. With data and transport models presently available, it is possible to make fate predictions about specific chemical contaminants only for the trace contaminant conditions described in zone 3. We must be able to make similar fate predictions about high concentrations.

Investigations need to be undertaken to explore the general behavior of flow and disperson of high concentration wastes in subsoils and in porous media. If these wastes are organic chemical-waste mixtures, they may have a bulk density greater or less than that of water. The leachate may be made up of two phases, an organic solvent phase and an aqueous phase. These phases may co-exist in both zones 1 and 2. Results of field studies suggest that an organic layer "floats" on the top of the aqueous phase in the groundwater aquifer. The present generation of predictive models that purport to quantify the flow and dispersion of chemical contaminants in groundwater cannot handle the above described density gradient and separate phase conditions. Our needs, then, include: first, laboratory simulation of the leachate migration process for high chemical concentrations to explore the qualitative features of the process and second, model reformulation based upon the observed mechanisms to account for the density stratification and the presence of two phases.

Some specific investigations are needed to explore the effect of high chemical concentrations on the transport processes. Specifically, how does density stratification or density dif-

ferences affect the natural diffusive/dispersive processes in porous media? Model concepts need be developed to relate the simultaneous flow of two liquid phases in a porous media and the interphase chemical transfer process. Are the conventional models that result in the retardation concept appropriate for zones 1 and 2, or are the "fixed-bed breakthrough" theory of adsorption and ion-exchange unit operations more appropriate?

In many respects, the bottom sediment of lakes and rivers is similar to saturated soils. Investigations of transport in this portion of the aquatic ecosystem have been made and are still under way; however, they have not dealt specifically with high chemical concentrations. Results of episodic spills or long term releases of hazardous chemicals can result in extreme contamination of bottom sediment. Layers of sediment, called "hot spots," are created. These deposits may be buried by fresher sediment creating a highly contaminated layer which can exist for long periods and slowly release its toxic constituents to the overlying water. In-sediment transport processes in both quiescent and flowing water need to be investigated by use of pilot-scale laboratory simulators. These simulators are to be of such dimensions that they contain the major natural influences that exist in the specific environment.

4.1.2. Transport processes in unsaturated soils

Research Recommendations

- °The effective diffusion coefficient for the gas phase and the liquid phase in unsaturated porous media
- °The convection processes in the liquid phase as driven both by the evaporation of water at the soil surface and the capillary forces from liquid waste buried below the surface
- °The convection processes in the gas phase as driven by internal gas generation (i.e., bio-gas), atmospheric pressure pumping, and water evaporation beneath the surface
- °Temperature gradients with associated energy flux rates within the top 30 to 50 cm of the surface

The conditions of unsaturated soils present an altogether different system that in many ways is much more complex than that of the saturated soils. Unsaturated conditions occur in both surface and subsurface soils, resulting in the presence of a gaseous phase. Important problems with regard to high concentrations of hazardous chemicals described in the body of the report include landfills, landfarms, and contaminated land. The latter has resulted mainly from decommissioned industrial sites.

Studies of some transport processes concerned with movement of trace contaminants in this terrestrial ecosystem have been made. There are virtually no studies available that address high chemical concentrations in the soil environment. Studies, both experimental and model development, of chemical transport mechanisms in unsaturated soils should involve laboratory investigations and simulations with the goal of isolating and quantifying the specific transport mechanisms. Based upon the quantitative and qualitative observations, appropriate mathematical models should

be proposed and verified based upon the equations of change. Due to the complexity of the transport processes, this work will undoubtedly involve specific chemicals in the waste and the water for each of the fluid phases with use of the multicomponent continuity equation, plus the equations of momentum and energy.

4.1.3. Transport processes on the fluid side of earthen interfaces

Research Recommendations

- The evaporation process, both natural convection and forced (i.e., wind enhanced) convection, of chemicals that exist in pure and mixed states on the surface of soil
- The mechanism and kinetics of dissolution of chemicals that exist in pure and mixed states on the surface of bottom sediments of lakes, rivers, and estuaries
- The deposition and re-entrainment of particles containing hazardous chemical constituents in the presence of fluid flow to cover both air and water regions above earthen surfaces

The fluid side of earthen interfaces is taken to mean the air boundary layer above soil surfaces and the water boundary layer above a bottom sediment surface.

Many aspects of chemical transport involving fluids near interfaces are very well understood and numerous models exist for obtaining reliable estimates of appropriate coefficients to quantify flux rates. This work typically reflects highly idealized, homogeneous, and regular interface regions. A lesser amount of work has been done which involves some of the more important complexities presented by the natural interfaces above soil and bottom sediment. The items recommended for research require additional investigations which should include high chemical con-

centration conditions.

4.2 Equilibrium Processes

4.2.1. Air-soil sorption processes

Research Recommendations

- °Equilibrium sorption on "air-dry" soils, including polar and nonpolar species in single, binary, and tertiary mixtures
- °Equilibrium sorption on moist soils concerning the behavior of equilibrium isotherms for water contents between "air-dry" and ca. 10% water (5 bars)
- °The role of cellulose-type material in the soil, disposed with organic chemicals
- °The physico-chemical nature of organic material at the waste disposal site

A comprehensive investigation of the equilibrium behavior of volatile chemicals on soil and subsoil systems needs to be performed. As was pointed out in the body of the report and in the scenario analysis, our understanding of the mechanisms of partitioning of volatile chemical species between the soil phase and the air phase is incomplete. Only the condition of low chemical concentrations in soils with water content of approximately 5% or higher is fairly well understood and quantifiable. It appears that, if the chemical concentration is low and if there is sufficient moisture, Henry's law applies and then an analytical relationship between chemical concentration (or partial pressure) in the soil-pore air and chemical concentration on the soil can be produced. However, even in this case few data exist for polar and nonpolar volatile organics.

Equilibrium sorption on "air-dry" soils: Single, binary, and tertiary mixtures should be studied and should include both polar and nonpolar species. The roles of the soil organic matter, clay content, clay type, temperature, inert gases (e.g., air, methane, and carbon dioxide) on sorption with "air-dry" soils need to be elucidated. Some evidence suggests that the partial vapor pressure of a chemical is reduced significantly if no soil water is present. This is particularly important for quantifying the appropriate partial pressure for so-called surface-applied chemicals since the top few millimeters of the soil surface can become essentially "air-dry" during some time intervals. It has been suggested that the BET (i.e., Brunauer, Emmett, and Teller) adsorption theory is applicable and should be considered as the model for interpreting the data.

Equilibrium sorption on moist soils: Water will most likely be present on soils, but not always present in sufficient quantities to form one or more mono-molecular layers on the soil surface. Consequently, the investigations should concern the nature of behavior of the equilibrium isotherms for the range of water contents between "air-dry" and approximately 10% water (5 bars), when the water molecules tend to compete for adsorption sites. Studies should involve polar and nonpolar substances and include the effect of soil organic matter, surface area, clay content, clay type, temperature, and inert gases. Ideally, mathematical models based upon equilibrium mechanisms should be produced as a means of extending the data and extrapolating them to other chemicals and soils.

The role of cellulose-type material incorporated in soil: Codisposal in the past has involved the mixing of volatile solid and liquid organic chemicals with domestic garbage, waste paper, hay, and other refuse in landfills as a means of "immobilizing" the waste. Investigations of the effect of such high concentrations of cellulose (i.e., 25 to 50%) type organic matter on the vapor pressure reduction need be performed.

Characterization of the physico-chemical nature of organic material (soil organic matter and various sludges) at the waste disposal site: Hazardous chemicals in high concentrations can be associated with three different types of soil organic matter: 1) natural organic matter produced from decayed biomass such as plant and animal debris, 2) bio-sludges produced from microbial cultures of wastewater treatment plants (e.g., activated sludge, anaerobic digesters), and 3) oil sludges from petroleum, petrochemical, or organic chemical manufacturing operations. Are these types of soil organic matter similar enough to be treated as a single parameter with respect to equilibrium considerations, or are they different in their sorptive properties, surface area, chemical structure, average molecular weight, and other influencial features? Raoult's law has been proposed as an equilibrium model for estimating chemical vapor pressures of volatile hydrocarbons in oily sludges. Is this an appropriate approach, and under what conditions can it be extended to the other types of soil organic matter and used for chlorinated substances such as PCB's?

4.2.2. Water-soil sorption processes

Research Recommendations

- °Equilibrium sorption on soil and bottom sediment of single organic species, both polar and nonpolar, in the high chemical concentration range or at the solubility limit of the chemical. The appropriateness of various isotherm model formulations needs to be evaluated.
- °Equilibrium sorption on soil of multicomponent organic mixtures with the combined concentration of all species at high concentrations in the presence and absence of organic matter.
- °Equilibrium sorption of high concentration of metals on soil and sediment.

A comprehensive investigation needs to be performed on the equilibrium partitioning of organic molecules, metal ions, and metal complex ions between soil and water. The kinetics of the partitioning process must also be studied. Much material is available in the literature on nonpolar organics at low concentrations, and algorithms have been published that allow one to predict reliable values of K_p (partition coefficients) based upon parameters such as chemical solubility, chemical melting point, and soil organic matter content. This approach, which is applicable to chemicals in both terrestrial and aquatic ecosystems, needs to be extended to cover a higher range of organic chemical concentrations, multicomponent chemical mixtures, metal ions, and complexes.

Studies of equilibrium sorption on soil and bottom sediment of single organic species, both polar and nonpolar, need to be extended to the high chemical concentration range or to the solubility limit of the chemical. If the chemical is infinitely

soluble, then a 5% solution is a reasonable upper boundary for investigation. If a separate phase forms prior to this limit, then investigations of concentrations up to the solubility are appropriate. Does the presence of the soil affect the ultimate solubility?

Most studies performed to date have been with surface soils which have relatively high organic matter content. Data on single component partition coefficients for subsoils need to be generated with the goal of obtaining an analytical expression that relates the partition coefficient to the chemical solubility, melting point, clay content, clay type, temperature, and other influences. Development of the appropriate correlations should be based upon sound physical chemistry concepts concerning the nature of chemical bonds and attraction forces for water and chemical molecules on the soil surfaces.

Studies need to be made on equilibrium sorption on soil of multicomponent organic mixtures with the sum total concentration of all species in the high concentration range. How does the presence of a high concentration of cyclohexane affect the partition coefficient of PCB? The prediction of key chemical concentrations in leachate plumes containing several organic chemicals moving through subsoils cannot be performed at present because of the lack of data and clear concepts of the physicochemical adsorption processes involving multicomponent leachates at high total chemical concentration in subsurface soils. Theoretical approaches such as proposed by Dexter and Pavlou

(1978) and Rao et al. (1983) seem appropriate as a starting point.

Studies of equilibrium sorption of high concentrations of various species of metals on soil need to be made. Metals can be present as ions, as complex ions, and in molecular form. What is needed is an algorithm based upon physical chemistry processes supported by data relating the partitioning of metal species between the pore water and the adjoining soil surface. Some of the factors of likely importance are valence of the ion, size of the ion, hydrodynamic radius, ion-exchange capacity of the soil (cationic or anionic), surface area, clay type, clay content, temperature, organic matter, and pH. These studies need to cover the entire concentration range and include the effects of the presence of organic compounds in the leachate.

4.3 Other Physico-Chemical Processes

Research Recommendations

- Measurement of alterations in chemical and physical properties created in artificial or unnatural mixtures and their influence on transport processes through a medium and an ecosystem

The presence of high chemical concentrations in aquatic and terrestrial ecosystems will undoubtedly alter the basic structure and properties of these natural environments to a greater or lesser extent. Much of the work that has been done with respect to transport and other processes in soil and sediment systems has been with the systems very near to the natural state. Where high chemical concentrations occur at disposal sites, treatment sites, abandoned sites,

or other locations, the presence of the foreign substance amounts to a considerable fraction of the sediment or soil and, therefore, can impart different or changed properties. In effect, we need to know more about the nature of these artificial and unnatural mixtures that are created.

These investigations will undoubtedly involve the re-creation of contamination events under controlled laboratory conditions with the subsequent measurement of properties and parameters related to transport processes in particular. The following is a list of important properties and parameters:

1. Residual saturation: the volume of soil or porous material necessary to immobilize a quantity of liquid spilled or otherwise placed on soil.
2. Porosity: the fraction of void space occupied by gases and fluids (air, water, organic matter, chemicals) in porous media of soils and bottom sediment.
3. Permeability: the ability of the porous media to transmit fluids under pressure; applies to both gases and liquids in soil and to liquids in bottom sediment.
4. Capillary rise: the ability of soil particles to become wetted by the fluids and sustain a height of fluid due the interfacial tension.

5. Reactive effects: alterations of the soil or sediment that occur due to irreversible adsorption or otherwise incorporation of waste into the particles, producing significant physical and chemical transformations which destroy or significantly alter the basic material. An example is the complete destruction of some clays by the presence of high organic chemical concentrations.

4.4 Transformation Processes

Research Recommendations

- °Assessment of microbial degradation under stress conditions (e.g. high chemical concentrations, oxygen-limited environment)
- °Abiotic transformation of chemicals at high concentrations and the effect of altered environmental conditions on these abiotic processes
- °Photochemical transformations (degradation and polymerization) of organic chemicals at high concentrations in various nonaqueous solvents
- °Transformation of organometallic complexes in sediment and soil

Numerous studies have been reported which deal with the transformations of organic chemicals in the environment. In general, most studies have been related to the microbial degradation of various pesticides. Incubation studies have been conducted under aerobic conditions, neutral pH values, optimum temperature regimes, and at low pesticide concentrations. In other words, conditions have been selected to maximize microbial degradation rates. However, conditions which exist in a hazardous waste landfill are not conducive to maximizing the degradation rate of most materials. Future research efforts need to be directed toward providing data which would allow a better assessment of microbial degradation processes under stress conditions.

An additional area of research which needs to be explored involves abiotic transformations of chemicals. At high concentrations, what chemical degradation reactions occur and what are the rates of transformation? Most pesticide studies have been conducted at low concentrations and many of the compounds are very complex in structure and reactivity.

A third research effort needs to be oriented towards additional studies of photochemical transformation of hazardous chemicals in soil and on the surface of aqueous systems. As before, many previous studies have used pesticides which may and may not be comparable to most hazardous organics. Neither will an aqueous system be appropriate. How will an organic solvent system influence photodecomposition of high concentrations of chemicals on the soil or water surface?

Microbial degradation of high concentrations of hazardous organic chemicals in an oxygen-limited environment: The microbial degradation rate of various organic compounds under anaerobic conditions would be expected to be much slower than under aerobic conditions especially for aromatic chemicals whose rapid degradation largely depends upon the presence of molecular oxygen.

Subsoil and sediment conditions of limited oxygen, low organic matter levels, high clay content, very low nitrogen levels, low microbial populations, and reduced temperatures would all act to limit the microbial degradation rate of organic chemicals. The biotic transformation rate of representative organic

chemicals under "non-optimal" conditions needs to be quantitated. The influence of parameters such as oxygen levels, nitrogen addition rates, and microbial inoculation on the degradation rates should be evaluated.

Many chemicals at low concentrations are degraded rapidly under optimal conditions, but degradation at high concentrations has not been investigated. High concentrations of such chemicals as phenol and chloroform are toxic to microorganisms, and thus, the degradation rates would most likely be concentration dependent and should be measured under various environmental conditions. It would also be desirable to measure the levels of various metabolites which may be formed. Information of the type proposed is needed for use in development and testing of mathematical models.

Abiotic transformations of high concentrations of hazardous organic chemicals in sediment and subsoil environments: Abiotic or chemical transformations of several pesticides have been shown to occur, but much less information is available on hazardous organic chemicals. In subsoil and sediment environments, the higher clay levels and resulting larger surface area compared to surface soil could facilitate a greater rate of abiotic transformation. Higher chemical concentration and the presence of potentially catalytic inorganic ions may also facilitate chemical reactions.

Because of the uniqueness of the environments, future studies need to be conducted to evaluate the influence of pH, Eh, clay content and type, surface area, temperature, moisture, various amounts and types of metal ions, organic chemical concentration, and type of organic chemical on the rate of abiotic chemical transformation. Specific abiotic transformations which are of concern include hydrolysis, polymerization, oxidation, and reduction reactions. Test methods should be developed for the various reactions, and the data should be incorporated into predictive models.

Photochemical transformation of hazardous organic chemicals: Before an organic chemical will undergo photochemical alteration, the chemical must absorb ultraviolet radiation. Thus, the chemicals to be investigated will most likely be surface applied to the soil. Photochemical degradation has been shown to be an important mechanism of pesticide dissipation, but data are far more limited for hazardous organic chemicals. Studies need to be conducted to evaluate the influence of radiation frequency and intensity on photochemical transformations of high concentrations of mixtures of organic chemicals in various nonaqueous solvents. Degradation as well as polymerization reaction kinetics need to be evaluated.

Transformation of organometallic complexes in sediment and soil: The codisposal of heavy metals and organic chemicals may lead to the formation of various organometallic chelates or complexes. Such chelates or complexes may facilitate the

transport of hazardous materials to a greater degree than expected and most likely have altered degradation characteristics. Studies need to be conducted to evaluate the kinetics of formation of various heavy metal organic chelates and/or complexes under conditions similar to landfills and sediments. The biotic and abiotic transformations of such chelates should be investigated under anaerobic conditions. Transport of chelates is also an important characteristic and appropriate sorption and transport studies should be conducted.

5.0 SUMMARY

There is considerable information available on the effects of trace chemical contaminants, such as pesticides, PCB's, chlorinated hydrocarbons, and metal ions in the respective ecosystems. Predictive techniques are becoming available to describe the transport and transformation of such contaminants and, thus, their fate and distribution in certain components of the environment. High chemical contaminant concentrations are those levels of application which a) are more easily expressed as a percentage (i.e., 5% or greater), and b) cause major characteristic (i.e., physical, chemical, or biological) changes in the soil or water.

Present predictive methods and models that trace the transport and transformation of chemical species are based upon "natural" soil and water properties such as density, porosity, infiltration, permeability, viscosity, hydrophobicity, and diffusivity. When the chemical contaminant is present in high concentrations, then the assumption of "natural" soil and water properties is very suspect. The major goal of this project was to assess the research needs that will address chemical contaminants present in high concentrations in terrestrial and aquatic ecosystems.

The twelve most important research areas in priority order are

Priority

1 °Assessment of microbial degradation rates and microbial activity under stress conditions in soil and water (e.g. high chemical contaminant concentrations and limited oxygen, limited nutrients, and/or limited microbial populations.)

2 °Abiotic transformations of chemicals at high concentrations and the effect of altered environmental conditions on these abiotic processes.

3 °Equilibrium sorption on soil and bottom sediment of single organic species, both polar and nonpolar, in the high chemical concentration range or at the solubility limit of the chemical. The appropriateness of various isotherm model formulations needs to be evaluated.

4 °Equilibrium sorption on soil of multicomponent organic mixtures with the combined concentration of all species at high concentrations in the presence and absence of organic matter.

5 °Formation, transformation, and transport of organometallic chelates and complexes in soil and sediment. The studies should also include equilibrium sorption of high concentrations of metals.

6 °Laboratory simulation of leachate migration processes (e.g., density stratification and two-phase flow) for high chemical concentrations. Model reformulation based upon the observed mechanisms to account for density stratification and the presence of two phases.

7 °Vapor equilibrium sorption on "air-dry" soils, including polar and nonpolar species in single, binary, and tertiary mixtures.

8 °Vapor equilibrium sorption on moist soils concerning the behavior of equilibrium isotherms for water contents between "air-dry" and ca. 10% water (5 bars).

9 °Transport processes in unsaturated soils including effective gas and liquid phase diffusivities, convection processes due to water and gas movement, processes driven by capillary forces, and temperature gradients.

10 °The deposition and re-entrainment of particles containing hazardous chemical constituents in the presence of fluid flow to cover both air and water regions above earthen surfaces.

11 °Develop solubility data for aqueous-organic liquids characteristic of high chemical concentrations appropriate to chemical waste landfill leachate and test existing solution models for validation purposes.

12 °Develop vapor pressure data for chemical waste and organic sludge (e.g., cellulose, biological, petroleum-petrochem) mixtures of high chemical concentration and test existing mixture models for validation purposes.

6.0 REFERENCES

Acar, Y., A. Hamidon, S. Field, and L. Scott. 1984. Organic fluid effects on hydraulic conductivity of compacted kaolinite. Annual Research Symp. U.S.EPA, Ft. Mitchell, KY. April, 1984.

Alexander, M. 1981. Biodegradation of chemicals of environmental concern. Science 211:132-138.

Altenbaumer, T., R. Kew, B. Matthews, and L. Wright. 1982. A study of contaminated soil volumes resulting from organic liquid spills. Senior Project Report, Dep. of Chem. Eng., Univ. of Arkansas, Fayetteville.

Alzaydi, A.A., C.A. Moore, and I.S. Rai. 1978. Combined pressure and diffusional transition region flow of gases in porous media. AIChE J. 24(1):35-43.

Anderson, D., K.W. Brown, and J. Green. 1982. Effect of organic fluids on the permeability of clay liners. Proc. 8th Ann. Res. Symp., Ft. Mitchell, KY. Land Disposal of Hazardous Waste, EPA-600/9-82-002. p. 179.

Armstrong, D.E. and J.G. Konrad. 1974. Nonbiological degradation of pesticides. p. 123-131. In W.D. Guenzi (ed.) Pesticides in soil and water. Soil Sci. Soc. Am. Madison, WI.

Ashworth, P. 1982. A dispersion model for sinker liquids spilled into waterways. Proc. 1982 Hazardous Matr. Spills Conf., Milwaukee, WI p. 404-413.

Avnimelech, Y. and A. Raveh. 1982. Decomposition of chelates leached from waste disposal sites. J. Environ. Qual. 11:69-72.

Bailey, G.W. and J.L. White. 1970. Factors influencing the

adsorption, desorption, and movement of pesticides in soil. Residue Rev. 32:29-92.

Boethling, R.S. and M. Alexander. 1979. Effect of concentration of organic chemicals on their biodegradation by natural microbial communities. Appl. Environ. Microbiol. 37:1211-1216.

Brown, D.S. and E.W. Flagg. 1981. Empirical prediction of organic pollutant sorption in natural sediments. J. Environ. Qual. 10:382-386.

Brown, K.W. and D. Anderson. 1980. Effect of organic chemicals on clay liner permeability. p. 123-134. Proc. Sixth Ann. Res. Symp. on Disposal Hazardous Waste. EPA-600/9-80-010.

Buddin, W. 1914. Partial sterilization of soil by volatile and non-volatile antiseptics. J. Agric. Sci. 6:417-451.

Callahan, M.A. 1979. Water-related environmental fate of 129 priority pollutants. Vol II, EPA-440/4-79-0296, Washington, DC, p. 44-1.

Cairney, T. 1982. In situ reclamation of contaminated land: the problem of a safe design. Public Health Eng. 10(4):215-218.

Christy, P.S. and L.J. Thibodeaux. 1982. Spill of soluble, high density, immiscible chemicals in rivers. Environ. Prog. 1(2):120.

Chiou, C.T., P.E. Porter, and D.W. Schmedding. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. Environ. Sci. Technol. 17(4):227.

Chou, S.J., B.W. Fisher, and R.A. Griffin. 1981. Aqueous chemistry and adsorption of hexachloropentadiene by earth

materials. P. 29 in Proc. 7th Ann. Res. Conf. - Land Disposal: Hazardous Waste, EPA-600/9-81-002.

Crosby, D.G. and C.S. Tang. 1969. Photodecomposition of 3-(p-chlorophenyl)-1,1-dimethylurea (monuron). J. Agric. Food Chem. 17:1041-1044.

Crosby, D.G. and A.S. Wong. 1977. Environmental degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Science 195:1337-1338.

Cupitt, L.T. 1980. Fate of toxic and hazardous materials in the air environment, EPA-600/3-80-084, U.S. Environmental Sciences Res. Lab, Research Triangle Park, NC p. 12-17.

Dean, J.A., ed. 1979. Lange's Handbook of Chemistry, 12th ed., McGraw-Hill, NY p. 10-28 to 10-54.

Dexter, R.N. and S.P. Pavlou. 1978. Distribution of stable organic molecules in the marine environment: Physical-chemical aspects chlorinated hydrocarbons. Marine Chem. 7:67-84.

Edgehill, R.U. and R.K. Finn. 1983. Microbial treatment of soil to remove pentachlorophenol. Appl. Environ. Microbiol. 45:1122-1125.

Enfield, C.G., R.F. Carsel, S.Z. Cohen, T. Phan, and D.M. Walters. 1980. Approximating pollutant transport to ground-water. R.S. Kerr, U.S.EPA, ORD, Ada, OK (Internal document).

Essex, J., Chairman. 1983. International land reclamation conference and exhibition - reclamation 83. Conf. Proc. Industrial Seminars Ltd., Kent, England.

Fannin, T.E., M.D. Marcus, D.A. Anderson, and H.L. Bergman.

1981. Use of a fractional factorial design to evaluate interactions of environmental factors affecting biodegradation rates. Appl. Environ. Microbiol. 42:936-943.

Fine, J.C. 1980. Toxic waste dangers. Water Spectrum 13:23-30.

Freeze, R.A. and J.A. Cherry. 1979. Groundwater, Prentice-Hall, Inc., Englewood Cliffs, NJ, p. 444-447.

Glotfelty, D.E., A.W. Taylor, and W.H. Zoller. 1983. Atmospheric dispersion of vapors: Are molecular properties unimportant? Science 219:843-845.

Grimes, D.J. and S.M. Morrison. 1975. Bacterial bioconcentration of chlorinated hydrocarbon insecticides from aqueous systems. Microbiol. Ecol. 2:43-59.

Havens, J.A. 1982. A review of mathematical models for prediction of heavy gas atmospheric dispersion. Inst. Chem. Eng. Symp. Ser. No.71, p. 1-24.

Healy, J.B. and L.Y. Young. 1979. Anaerobic biodegradation of eleven aromatic compounds to methane. Appl. Environ. Microbiol. 38:84-89.

Horn, E.G., L.J. Hetling, and T.J. Tofflemire. 1979. The problem of PCB's in the Hudson River System. p. 591-609. In W.J. Nicholson and J.A. Moore (ed.) Health effects of halogenated aromatic hydrocarbons. New York Academy of Sciences, NY.

Jurinak, L.S. and D.H. Volman. 1957. Application of the Brunauer, Emmett and Teller equation to ethylene dibromide adsorption by soils. Soil Sci. 83:487.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of

hydrophobic pollutants on natural sediments. Water Res. 13:241-248.

King, M.B. 1969. Phase Equilibrium in Mixtures. Pergamon Press Ltd., Oxford p. 239-255.

LaFleur, K. 1973. Fluometuron-soil-solvent interactions. Soil Sci. 116:376-381.

Letey, J. and W.J. Farmer. 1974. Movement of pesticides in soil. p. 67-97. In W.D. Guenzi (ed.) Petsicides in soil and water. Soil Sci. Soc. Am., Madison, WI.

Lindsay, W.L. 1972. Inorganic phase equilibria of micronutrients in soils. p. 41-57. In J.J. Mortvedt (ed.) Micronutrients in Agriculture. Soil Sci. Soc. Am., Inc., Madison, WI.

Lisk, D.J. 1972. Trace metals in soils, plants, and animals. Adv. Agron. 24:267-325.

Martin, J.P. 1972. Side effects of organic chemicals on soil properties and plant growth. p. 733-792. In C.A.I. Goring and J.W. Hamaker (ed.) Organic chemicals in the soil environment. Marcel Dekker, Inc., New York.

Martin, J.P., K. Haider, and E. Bondietti. 1972. Properties of model humic acids synthesized by phenoloxidase and autoxidation of phenols and other compounds formed by soil fungi. Proc. Int. Meet. Humic Substances. Pudoc, Wageningen. p. 171-186.

McOmber, R.M., C.A. Moore, J.W. Massmann, and J.J. Walsh. 1982. Verification of gas migration at Lee's Lane landfill. Proc. 8th Ann. Res. Symp. - Land Disposal of Hazardous Waste,

EPA-600/9-82-002, p. 150-160.

Mills, A.C. and J.W. Biggar. 1969. Solubility-temperature effect on the adsorption of gamma and beta BHC from aqueous and hexane solutions by soil materials. Soil Sci. Soc. Am. Proc. 33:210-216.

Moore, C.A., I.S. Rai, and A.A. Alzaydi. 1979. Methane migration around sanitary landfills. Geotechnical Engineering Division, Proc. Amer. Soc. Civil Eng. 105(GT2):131-145.

Norman, C. 1983. Wastes seep round the law. Science 220:34.

Norvell, W.A. 1972. Equilibria of metal chelates in soil solution. p. 115-138. In J.J. Mortvedt (ed.) Micronutrients in Agriculture. Soil Sci. Soc. Am., Inc., Madison, WI.

Orndorff, S.A. and R.R. Colwell. 1980. Distribution and characterization of kepone-resistant bacteria in the aquatic environment. Appl. Environ. Microbiol. 39:611-622.

Ou, L.T., J.M. Davidson, and D.F. Rothwell. 1978. Response of soil microflora to high 2,4-D applications. Soil Biol. Biochem. 10:443-445.

Overcash, M.R. and D. Pal. 1979. Design of Land Treatment Systems For Industrial Wastes-Theory and Practice. Ann Arbor Sci. Publishers, Inc., Ann Arbor, MI. p. 221-333.

Pal, D., M.R. Overcash, and P.W. Westerman. 1977. Plant-soil assimilative capacity for organic solvent constituents in industrial wastes. p. 259-271. Proc. 32nd Purdue Ind. Waste Conf.

Paris, D.F., D.L. Lewis, and J.T. Barnett, Jr. 1977. Biocon-

centration of toxaphene by microorganisms. Bull. Environ. Toxicol. 17:564-572.

Paris, D.F., W.C. Steen, G.L. Baughman, and J.T. Barnett, Jr. 1981. Second-order model to predict microbial degradation of organic compounds in natural waters. Appl. Environ. Microbiol. 41:603-609.

Parr, J.F. 1974. Effects of pesticides on microorganisms in soil and water. p. 315-340. In W.D. Guenzi (ed.) Pesticides in soil and water. Soil Sci. Soc. Am., Madison, WI.

Parr, J.F. and S. Smith. 1973. Degradation of trifluralin under laboratory conditions and soil anaerobiosis. Soil Sci. 115:55-63.

Percich, J.A. and J.L. Lockwood. 1978. Interactions of atrazine with soil microorganisms. Population changes and accumulation. Can. J. Microbiol. 24:1145-1152.

Perry, R.H. and C.H. Chilton. 1973. Chemical Engineer's Handbook, 5th ed., McGraw-Hill Book Company, NY.

Phillips, C.R. and J.S. Nathwani. 1977. Development of a soil-waste interaction matrix for assessing land disposal of industrial wastes. Water Res. 11:859-868.

Plimmer, J.R. 1970. The photochemistry of halogenated herbicides. Res. Rev. 33:47-74.

Pinnavaia, T.J., P.L. Hall, S.S. Cady, and M.M. Mortland. 1974. Aromatic radical cation formation on the intracrystal surfaces of transition metal lattice silicates. J. Physical Chem. 78:994-999.

Pye, V.I. and R. Patrick. 1983. Groundwater contamination in the United States. Science 221:713-718.

Rao, R.S.C., A.G. Hornsby, and P. Nkedi-Kizza. 1983. Influence of solvent mixtures on sorption and transport of toxic organic compounds in the subsurface environment. Paper 67, Env. Chemistry, Amer. Chem. Soc. Mtg., Washington, D.C., Aug. 28 - Sept. 2, 1983.

Raymond, R.L., J.O. Hudson, and V.W. Jamison. 1976. Oil degradation in soil. Appl. Environ. Microbiol. 31:522-535.

Reid, R.C., J.M. Prausnitz, and T.K. Sherwood. 1977. The Properties of Gases and Liquids, 3rd ed. McGraw-Hill Book Company, NY p. 368-384.

Sims, R.C. and M.R. Overcash. 1983. Fate of PNAs in soil-plant systems. Residue Rev. 88:1-68.

Saxena, J. and P.H. Howard. 1977. Environmental transformation of certain metals. Adv. Appl. Microbiol. 21:185-226.

Scott, H.D., D.C. Wolf, and T.L. Lavy. 1982. Apparent adsorption and microbial degradation of phenol by soil. J. Environ. Qual. 11:107-112.

Scott, H.D., D.C. Wolf, and T.L. Lavy. 1983. Adsorption and degradation of phenol at low concentrations in soil. J. Environ. Qual. 12:91-95.

Solomon, D.H., B.C. Loft, and J.D. Swift. 1968. Reactions catalyzed by minerals IV. The mechanism of the benzidine blue reaction on silicate minerals. Clay Minerals 7:389-397.

Spencer, W.F., W.J. Farmer, and W.A. Jury. 1982. Review:

Behavior of organic chemicals at soil, air, water interfaces as related to predicting the transport and volatilization of organic pollutants. Environ. Toxicol. Chem., 1:17-26.

Sposito, G. and S.V. Mattigod. 1979. GEOCHEM: A computer program for calculating chemical equilibria in soil solutions and other natural water systems. Kearney Foundation Soil Sci., Univ. California, Riverside.

Springer, C. 1979. Evaporation and disperson of hazardous materials. Final Report, Department of Air Force, Air Force Office of Scientific Research, No. AFOSR 78-3559.

Springer, C. and L.J. Thibodeaux. 1982. Emission of hazardous chemicals from surface and near surface impoundments into air. U.S.EPA/MERL, CR-8081612-02-0.

Stojanovic, B.J., M.V. Kennedy, and F.L. Shuman, Jr. 1972. Edaphic aspects of the disposal of unused pesticides, pesticide wastes, and pesticide containers. J. Environ. Qual. 1:54-62.

Sun, M. 1983. Missouri's costly dioxin lesson. Science 219:367-369.

Tanaka, F.S. and R.G. Wien. 1973. Hydrolysis of aqueous solutions of sodium 2,2-dichloropropionate under self-induced alkaline conditions. J. Agric. Food Chem. 21:285-288.

Thibodeaux, L.J. 1977. Mechanisms and idealized dissolution modes for high density (p>1), immiscible chemicals spilled in flowing aqueous environments. AIChE J. 23:544-554.

Thibodeaux, L.J. 1979. Chemodynamics-Environmental Movement of Chemicals in Air, Water, and Soil. J. Wiley, New York. p. 10-13.

Thibodeaux, L.J. 1981. Estimating the air emission of chemicals from hazardous waste landfills. J. Hazard. Matr. 4:235-244.

Thibodeaux, L.J. and B. Becker. 1982. Chemical transport rates near the sediment in wastewater impoundments. Environ. Prog. 1(4): 296.

Thibodeaux, L.J., Li-Kow Chang, and D.J. Lewis. 1980. Dissolution rates of organic contaminants located at the sediment interface of rivers, streams and tidal zones. In R.A. Baker (ed.) Contaminants and Sediments, Vol. 1, Ann Arbor Ser., Ann Arbor, MI p. 349-371.

Thibodeaux, L.J. and S.T. Hwang. 1982. Landfarming of petroleum waste-modeling the air emission problem. Environ. Prog. 1(1):42-46.

Thibodeaux, L.J. and H.D. Scott. 1984. Environmental exposure from chemicals, Chapter 4 - Air/Soil Exchange Coefficients, CRC Press, Inc., Boca Raton, FL. (in press)

Thibodeaux, L.J., C. Springer, and L.M. Riley. 1982. Models of mechanisms for the vapor phase emission of hazardous chemicals from landfills. J. Hazard. Matr. 7:63-74.

Van Engers, L. 1978. Mineralization of organic matter in the subsoil of a waste disposal site: a laboratory experiment. Soil Sci. 126:22-28.

Varga, J.M. and H.Y. Neujahr. 1970. Isolation from soil of phenol-utilizing organisms and metabolic studies on the pathways of phenol degradation. Plant Soil 33:565-571.

Wahid, P.A., C. Ramakrishna, and N. Sethunathan. 1980.

Instantaneous degradation of parathion in anaerobic soils. J. Environ. Qual. 9:127-130.

Walker, W.W. and B.J. Stojanovic. 1973. Microbial versus chemical degradation of malathion in soil. J. Environ. Qual. 2:229-232.

Wallace, J.R. 1982. Review of ground-water models. American Petroleum Institute, Washington, DC. p. 69.

Wang, T.S.C., S.W. Li, and Y.L. Ferng. 1978a. Catalytic polymerization of phenolic compounds by clay minerals. Soil Sci. 126:15-21.

Wang, T.S.C., S.W. Li, and P.M. Huang. 1978b. Catalytic polymerization of phenolic compounds by a latosol. Soil Sci. 126:81-86.

Wang, T.S.C., M.M. Kao, and P.M. Huang. 1980. The effect of pH on the catalytic synthesis of humic substances by illite. Soil Sci. 129:333-338.

Wang, W.C., G.F. Lee, and D. Spyridakis. 1972. Adsorption of parathion in a multicomponent solution. Water Res. 6:1219-1228.

Warner, P.H., J.M. Cohen, and J.C. Ireland. 1980. Determination of Henry's Law Constant of Selected Priority Pollutants. Municipal Environmental Research Laboratory, Office of Research and Development, U.S.EPA, Cincinnati, OH. p. 14.

Weber, J.B. and S.B. Weed. 1974. Effects of soil on the biological activity of pesticides. p. 223-256. In W.D. Guenzi (ed.) Pesticides in soil and water. Soil Sci. Soc. Am., Madison, WI.

Willis, G.H., R.C. Wander, and L.M. Southwick. 1974.

Degradation of trifluralin in soil suspensions as related to redox potential. J. Environ. Quality 3:262-265.

Winograd, I.J. 1981. Radioactive waste disposal in thick unsaturated zones. Science 214:1457-1464.

Worm, B.G., E.J. Dantin, and R.K. Seals, (eds.) 1981. Proc. Symp. and Workshop on Hazardous Waste Management, Louisiana State Univ., Baton Rouge, Nov. 16-20.

7.0 GLOSSARY

Glossary of terms used in the report.

advection - The process of conveyance of an atmospheric property solely by the mass motion of the atmosphere. Also applied to aqueous systems.

*__aerobic__ - Having molecular oxygen as a part of the environment.

*__air-dry__ - The state of dryness (of a soil) at equilibrium with the moisture content in the surrounding atmosphere. The actual moisture content will depend upon the relative humidity and the temperature of the surrounding atmosphere.

*__anaerobic__ - The absence of molecular oxygen or occurring in the absence of molecular oxygen (as a biochemical process).

binary mixture - A liquid containing two substances that are miscible.

biogas - Gas, usually methane and carbon dioxide, formed during anaerobic decomposition of organic wastes.

bottom sediment - Sediment located at the bottom of a waterbody.

*__cation-exchange capacity (CEC)__ - The sum of exchangeable cations that a soil, soil constituent, or other material can adsorb at a specific pH. It is usually expressed in milliequivalents per 100 grams of exchanger.

chemical contaminant - a chemical substance that makes (water or soil) inferior or impure by admixture, makes unfit for use by the introduction of unwholesome or undesirable elements or compounds.

codisposal - The process of mixing of municipal waste and industrial waste at the same time and place, usually in a landfill.

contaminated land - Land containing mixtures of chemicals originating from previous manufacturing operations on the site.

convection - Conveyance of a substance in which the fluid as a whole is moving.

creosote - A colorless or yellowish oily liquid containing a mixture of phenolic compounds obtained by distillation of coal tar.

diffusivity - The weight of a material, in grams, diffusing across an area of 1 square centimeter by molecular processes in one second in a unit concentration gradient.

---

*Specific terms relating to soil science are taken from the Glossary of Soil Science Terms, 1979, Soil Science Society of America, Madison, Wisconsin.

dispersion - The combined movement of a substance by molecular and turbulent processes in a fluid attributed to a concentration gradient, similar to molecular diffusion.

dispersivity - Similar to a dispersion coefficient.

dry soil - Soil void of free water.

dump site - Any site onto which waste has been placed.

hazardous waste - dangerous discards generated from our highly industrialized, technologically based society; refers to any waste or combination of wastes that presents or poses potential dangers to human health and safety or to living organisms in our environment; such wastes are lethal, non-degradable or may be biologically magnified, capable of promoting detrimental cumulative effects as well as short-term hazards; toxic chemicals, flammable, radioactive, explosive, or biological in nature and take the form of solids, sludges, gases or liquids.

*__humic acid__ - The dark-colored fraction of the soil humus which can be extracted with dilute alkali and is precipitated by acidification to pH 1-2. Exchange acidity at pH 7 usually varies from 200 to 400 meq/100 g.

immiscible - Pertaining to liquids that will not mix with each other.

land treatment - Operation of sludge or liquid waste degradation by spreading and incorporating into surface soil to promote biological activity.

landfarming - See land treatment.

landfill - Disposal of solid waste by burying in layers of earth in low ground.

landfill cell - A portion of a landfill partitioned off to contain a waste of a specific type or quantity.

mass flow - The mass of a fluid in motion which crosses a given area in a unit time.

miscible - Referring to liquids that are mutually soluble, that is, they will dissolve in each other.

mixture - A portion of matter consisting of two or more components in varying proportions that retain their own properties.

municipal sludge - See sewage sludge.

partial pressure - The pressure that would be exerted by one component of a mixture of gases if it were present alone in a container.

permeability - The ability of a membrane or other material to permit a substance to pass through it. The capacity of a porous rock, soil, or sediment for transmitting a fluid without damage to the structure of the medium.

petroleum sludge - Viscous liquids, semi-solids and solids with high water content from refinery operations usually still bottoms, tank bottoms, API separator, and filter media.

*__pH, soil__ - The negative logarithm of the hydrogen-ion activity of a soil. The degree of acidity (or alkalinity) of a soil as determined by means of a glass, quinhydrone, or other suitable electrode or indicator at a specified moisture content or soil-water ratio, and expressed in terms of the pH scale.

phase - Portion of a physical system (liquid, gas, solid) that is homogeneous throughout, has definable boundaries and can be separated physically from other phases.

porosity - The fraction as a percent of the total volume occupied by minute channels or open spaces.

retardation factor - The ratio of water velocity to the velocity of trace chemical dissolved in water as they move together through a porous formation.

saturated soil - Soil with all pore spaces occupied with water.

sewage sludge - A semiliquid waste with a solid concentration in excess of 2500 parts per million, obtained from the purification of municipal sewage.

sludge - Residue left after acid treatment of petroleum oils. Any semisolid waste from a chemical process.

*__soil__ - The unconsolidated mineral matter on the surface of the earth that has been subjected to and influenced by genetic and environmental factors of: parent material, climate (including moisture and temperature effects), macro- and microorganisms, and topography, all acting over a period of time and producing a product-soil-that differs from the material from which it is derived in many physical, chemical, biological and morphological properties, and characteristics.

*__soil organic matter__ - The organic fraction of the soil. Includes plant, animal, and microbial residues, fresh and at all stages of decomposition, and the relatively resistant soil humus.

soil water - Moisture in the soil.

solubility - The ability of a substance to form a solution with another substance.

solvent - That part of a solution that is present in the largest amount, or the compound that is normally liquid in the pure state (as for solutions of solids or gases in liquids).

subsoil - Soil underlying surface soil.

surface applied - An act of placing a chemical substance on the surface of the soil.

surface impoundment - A basin position on the ground without a cover containing liquid and/or solid waste.

surface soil - See soil.

tertiary mixture - A liquid containing three substances that are miscible.

toxic substance - a poison; a substance that through its chemical action usually kills, injures, or impairs an organism.

transport process - The conveyance of substances from point-to-point in space due primarily to gradients of intensive properties.

two-phase flow - The simultaneous movement of gas and liquid through a conduit, usually in the same direction.

unsaturated soil - Soil with pore spaces containing water and air or other gases.

vapor density - Concentration of a gas in a mixture based upon its partial or vapor pressure.

vapor pressure - For a liquid or solid, the pressure of the vapor in equilibrium with the liquid or solid.